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CERTAIN INTERFACIAL TENSION EQUILIBRIA IMPORTANT IN FLOTATION

By

WILL H. COGHILL AND CARL O. ANDERSON

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CERTAIN INTERFACIAL TENSION EQUILIBRIA IMPORTANT IN FLOTATION.

By WILL H. COGHILL AND CARL O. ANDERSON.

PART I.—THE EQUILIBRIUM OF THE INTERFACIAL TENSION FORCES OF TWO LIQUIDS AND A GAS.

INTRODUCTION.

The successful use of flotation for separating ores and the uncertainties surrounding the observed facts have resulted in an extensive literature. As a consequence many physical and chemical principles that otherwise would have been regarded as foreign to the metallurgical field have been called to attention and offered in explanation of the phenomena observed.

Some idea of the tremendous importance of flotation as an industrial process is obtained from the fact that in 1918 it was utilized in treating some 70 million tons of ore.[1] However, although this process profoundly influences modern practice in ore concentration, knowledge regarding it is largely empirical. For this reason writers have studied some of the principles often mentioned in the literature.

In the following pages the author discusses the graphic analysis of the interfacial forces acting at the common meeting line of three immiscible fluids (a gas, such as air, being regarded as one of the fluids) in contact with each other.

THE NEUMANN EQUILIBRIUM TRIANGLE OF INTERFACIAL TENSIONS.

Maxwell,[2] in the Encyclopedia Britannica, probably treats the subject of capillarity more fully than any other writer. He discusses the Neumann triangle as follows:

> If the three fluids can remain in contact with one another, the sum of any two of the quantities (interfacial tensions) must exceed the third, and by Neumann's rule the directions of the interfaces at the common edge must be

---

[1] Broadridge, Walter, Froth flotation: Bull. Inst. Min. and Met. No. 184, Jan., 1920, p. 1.

[2] Maxwell, J. C., Capillarity: Encyclop. Brit., 11th ed., 1910, vol. 5, p. 263.

> **parallel to the sides of a triangle, taken proportional to Aab, Bbc, Cca. (See fig. 1.) If the above-mentioned condition is not satisfied, the triangle is imaginary, and the three fluids can not rest in contact; the two weaker tensions, even if acting in full concert, being incapable of balancing the strongest.**

As regards the first part of the above quotation, the well-known algebraic formula, $\cos C=\frac{b^2+a^2-c^2}{2ab}$, may be applied to determine the angles of the triangle; that is, it is easy to determine graphically the angle that is analogous to the angle of contact of a liquid meeting a solid.

EXPERIMENTAL WORK.

In the present investigation preliminary experiments soon demonstrated that some pure liquids form lenses on pure water. When this condition obtains, the three interfacial forces acting may be represented as the sides of a Neumann triangle—force diagram—then by geometry the angles existing between the pairs of these forces are known. Further experimental work followed to study the configuration of lenses of one liquid lying upon another; from observed measurements values for the angles between the interfacial forces were calculated. These calculated angles are compared with the corresponding ones existing in the Neumann force triangle.

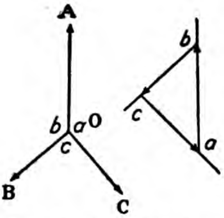

FIGURE 1.—The Neumann triangle.

Among the liquids that form lenses on water is paraffin oil. Langmuir[3] says that oils which do not contain active groups—as, for example, pure paraffin oil—do not spread on the surface of water. Lycopodium powder spread on the surface of water remained undisturbed during the addition of the oil, thus affording proof that the oil did not form a film on the water before making the lens. This precaution was consistently applied throughout the experiments. Carbon tetrachloride and carbon bisulphide at first glance seem to spread on water, but in reality the vapors pass into the air and settle on the water, thus affecting the lycopodium powder. The liquids themselves do not spread. A spreading liquid is manifested by an instantaneous effect that drives the powder to the wall of the dish, whereas the effect of the vapors mentioned is only local. Nonspreading oils when closeted with flotation oils are likely to absorb vapors through the stopper and become spreading oils.

When paraffin oil is placed on water, the tensions acting perpendicular to the line of contact of these fluids may be diagramed as shown in A, Figure 2, where *a* represents air; *o*, oil; and *w*, water.

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[3] Langmuir, Irving, The constitution of liquids, with especial reference to surface tension phenomena: Met. and Chem. Eng., vol. 15, 1916, p. 469.

The drop-weight method, as described in another article,[4] was used to obtain the values of the three tensions represented in the figure.

PARAFFIN OIL, WATER, AND AIR.

The first work was, therefore, with paraffin oil and water. Paraffin oil of the highest medicinal purity and distilled water were used. These liquids, so far as has been determined, are immiscible in each other.

The values of the tensions as determined, in grams per centimeter, are:

$$T_{w,a}=0.0730;\ T_{w,o}=0.0549;\ \text{and}\ T_{o,a}=0.0301.$$

These values can be converted into dynes per centimeter by multiplying by 981. All the experiments in this paper were performed at a temperature of about 22° C.

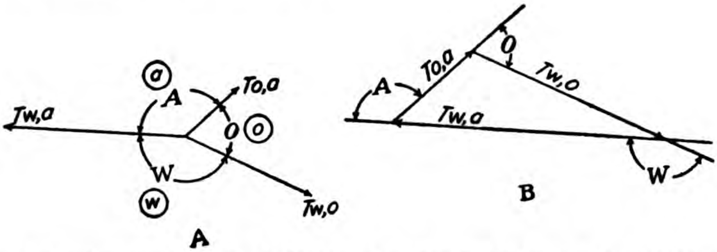

FIGURE 2.—Equilibrium triangle of the forces of interfacial tension in a plane perpendicular to the common meeting line of three fluids.

As no one of the three forces is greater than the sum of the other two, a force triangle may be constructed, as in B, Figure 2. The value of the sides of the triangle being known, the angles can readily be calculated by means of the cosine formula. On referring to B, Figure 2, it may be seen that

$$\cos\,(180°-A)=\frac{(T_{o,a})^2+(T_{w,a})^2-(T_{w,o})^2}{2(T_{o,a})\ (T_{w,a})}\,.$$

In a similar manner, angles $(180°-O)$ and $(180°-W)$ are determined. The angles obtained were

$$A=137°\ 10';\ O=64°\ 50';\ W=158°\ 00'.$$

After the air, water, and oil angles had been calculated from tensions obtained from results of the drop-weight method, cathetometer observations of floating lenses were made. The data obtained by means of the cathetometer were used to calculate the angles between the tensions and these were compared with those determined by the cosine formula. The obtained data were also used in drawing the exact shape of liquid lenses, for on their exact configuration no information has been found in the literature.

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[4] Coghill, W. H., Molecular forces in flotation: Min. and Sci. Press, vol. 116, June 1, 1918, p. 747.

The cathetometer had a vernier scale graduated to 0.005 cm.; the focal distance of the instrument was about 3 feet. All measurements were made in a vertical plane at right angles to the line of sight of the instrument.

PROCEDURE.

One of the liquids, as water, was placed in a crystallizing dish, 17 cm. in diameter. The oil was delivered to the water surface from a burette, and care was taken that each drop should fall on the oil lens formed by the previous drops. If the drops of oil struck the water surface first and then coalesced, the lens would be flatter, because of the tendency for traces of water and other impurities to be drawn into the interior of the lens. Thus the lens would not be pure oil, as it is when the drops coalesce on falling.

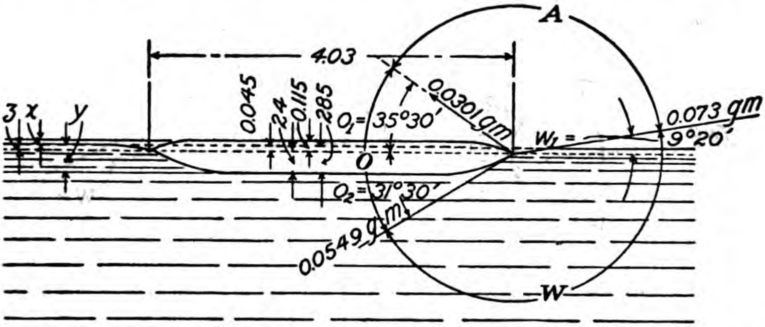

FIGURE 3.—Vertical section of a floating lens of paraffin oil with dimensions as shown in 10, Table 1.

On account of the effect of the water meniscus on the walls of the dish, two sets of cathetometer readings were necessary. In the first set the dish was overfilled, so that the water surface curved downward; then the difference in elevation of the top of the paraffin lens and the surface of the water was determined. This difference gives the value of x (See Table 1 and also Fig. 3). In the second set of readings some of the liquid was withdrawn from the dish, so that it was only partly filled, and the water meniscus curved upward. Readings were taken on the bottom of the paraffin lens and on the surface of the water; the difference gives the value of y. Finally, readings were made on the surface of the water and on the common meeting line of the three fluids; their difference gives the value of z.

PRECAUTIONS.

Certain important precautions were taken in making the above measurements.

A large dish was used, for at least three reasons: (1) The horizontal water surface must be large enough to permit study of a fairly large oil lens. Also, with too small a dish the curvature of the water meniscus would cause error in sighting on the horizontal part of the water surface; if the dish were very small, the lens would be riding on a slightly curved surface. (2) The dish should accommodate a lens so large that the curvature of the oil and water surfaces will be such that they may be dealt with mathematically by considering only one principal (vertical) plane of bending;[5] the second principal (horizontal) plane of bending may be disregarded if the lens is fairly large. (3) In a large dish a small part of its side is practically plane and does not produce distortions of the images. A thin-walled rectangular dish presenting a true plane surface through which to sight would have served much better, but one was not readily available.

A large lens has to be used for comparison of the angles calculated from cathetometer measurements with those obtained from the force triangle. As stated above (reason 2), a small lens has two principal planes of bending with corresponding radii of curvature; as the diameter of the lens increases, one of these radii rapidly approaches infinity, and may be neglected, because its reciprocal enters into the equation used later in calculating the angles. Thus the profile of a fairly large drop in a vertical section through its center is practically the same as that of a liquid when it meets a plane solid surface.

---

[5] Plane of bending is a term commonly used by Edser in his Textbook of Physics for Students.

TABLE 1.—*Calculated values of the air, oil, and water angles, A, O, and W, respectively, from cathetometer observations on paraffin-oil lens (sp. gr. 0.85) floating on water.*

(By equilibrium triangle, A=137° 10′, O=64° 50′, W=158°, 00′, where the sides are $T_{o,a}$=0.0301, $T_{w,a}$=0.073 and $T_{w,o}$=0.0549 gram per cm.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
No. of lens.	Volume of lens.	Vertical dimensions.				85/100 total thickness.	Diameter of lens.	*A*	*O*	*W*	O_1	O_2	W_1
		x	*y*	*z*	(*x*+*y*)								
	C. c.	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*
1	0.52	0.045	0.210	0.030	0.255	0.216	2.10	150 40	47 20	162 00	....	....	....
2	.62	.055	.240	.030	.295	.250	2.15	150	....	....	....	....	....
3	.78	.060	.265	.030	.325	.276	2.30	146 00	55 00	159 00	....	....	....
4	.88	.060	.275	.040	.335	.284	2.42	....	....	....	....	....	....
5	.94	.065	.280	.045	.345	.293	2.45	....	....	....	....	....	....
6	.99	.055	.270	.045	.325	.276	2.48	....	....	....	....	....	....
7	1.04	.055	.285	.040	.340	.289	2.55	142 10	60 40	157 10	....	....	....
8	1.14	.060	.280	.045	.340	.289	2.80	....	....	....	....	....	....
9	1.30	.055	.260	.045	.315	.267	2.98	140 30	60 00	159 30	....	....	....
10	2.60	.070	.285	.045	.355	.301	4.05	135 10	67 20	157 30	35 30	31 50	9 20

RESULTS.

The values of x, y, and z, obtained from cathetometer measurements, for a number of lenses are shown in Table 1. Figure 3 shows for a given lens (No. 10) the distance corresponding to x, y, and z; it also shows the angles A, O, and W, whose values appear in the table as calculated from cathetometer observations.[6] It should be noted that the diameter of the lenses studied were 2.10 cm. to 4.05 cm.; as the diameter increased the calculated angles A, O, and W agreed more closely with the corresponding angles of the equilibrium triangle. For a diameter greater than 4.0 cm., the second principal plane of bending has very little influence on the contour of the lens.

CALCULATION OF ANGLES.

The values of the angles W_1, O_1, and O_2, in Figure 3, are first calculated after which the angles A, O, and W are readily obtained.

The angles W_1 and O_1 may be calculated in two ways. First, (for W_1) consider the horizontal equilibrium of that part of the water (to the right) from the bottom of the dimple to the plane surface of the water. Let h be the head of water from its surface to the bottom of the dimple. The forces acting to the right over unit length at right angles to the paper are the forces restraining the head of water, $h\times\frac{h}{2}$, and the horizontal component of the water tension, as this tension is acting tangent to the profile of the water surface. Opposed to these forces is the surface tension of the water. Let T represent this tension; then the equation,

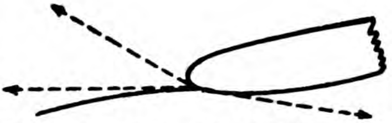

FIGURE 4.—Profile of a paraffin-oil lens floating on water. (After Hardy.) The dotted lines, representing the interfacial tensions, have been added.

$$h\times\frac{h}{2}+\mathrm{T}\cos W_1=\mathrm{T}, \tag{1}$$

may be written.

Simplifying,
$$\mathrm{h}=2\sqrt{\mathrm{T}}\sqrt{\frac{1-\cos W_1}{2}}, \text{ whence,}$$

$$\mathrm{h}=2\sqrt{\mathrm{T}}\sin\frac{W_1}{2}. \tag{1'}$$

---

[6] Hardy (Proc. Roy. Soc., London, Ser. A, 1912, vol. 86, p. 633) draws a sketch of a paraffin-oil lens on water. He says: "Careful examination of the lens shows that the water-air surface is drawn under its edge. The contour of a large flat-topped lens, 2 or 3 cm. in diameter, is somewhat as shown in Figure 4."

If the force lines were drawn representing the tensions tangent to the surfaces at the common point of meeting it would be seen that the water tension and the oil tension (72 + 30) would be acting in almost the opposite direction to the oil-water tension (55). There could not be equilibrium when the water is drawn under the paraffin lens as Hardy shows it.

But h is equal to z, then for No. 10 in Table 1,

$$z = 0.045 = 2\sqrt{0.073}\ \sin\frac{W_1}{2}$$

$$W_1 = 9^\circ\ 20' \text{ (see Table 1, last column).}$$

Either equation 1 or 1′ may be used in this calculation.

The angle 0_1 may be calculated in the same way. However, the value of $\frac{h^2}{2}$ must be multiplied by 0.85, the specific gravity of paraffin oil.

The second method of calculating these angles depends upon the differential of the equation of the curve of the liquid surface. The equation,[7] which has been discussed in some detail by the writers in another paper is

$$x = \pm(4a^2 - y^2)^{\frac{1}{2}} \pm a \log\frac{2a + (4a^2 - y^2)^{\frac{1}{2}}}{y} + C,$$

where $a = \sqrt{\frac{T}{d}}$, in which T is the tension in grams per cm. and d is the specific gravity of the liquid. Differentiating for one quadrant of the curve, the upper right hand quadrant,

$$\frac{dx}{dy} = \frac{y}{(4a^2 - y^2)^{\frac{1}{2}}} - \frac{2a^2}{y(4a^2 - y^2)^{\frac{1}{2}}}.$$

Let θ be the angle of inclination of the tangent to the x-axis, then taking the reciprocal of the differential, there is obtained,

$$\frac{dy}{dx} = \tan\theta = y\frac{(4a^2 - y^2)^{\frac{1}{2}}}{y^2 - 2a^2}.$$

Squaring and replacing $\tan^2\theta$ by $(\sec^2\theta - 1)$, the following equation is obtained:

$$\sec^2\theta = \frac{y^2(4a^2 - y^2) + y^4 - 4a^2y^2 + 4a^4}{(y^2 - 2a)^2}.$$

Reducing,

$$y^2 - 2a^2 = -2a^2\cos\theta,$$

and

$$y = 2a\sin\tfrac{1}{2}\theta. \qquad (2)$$

This expression is identical with equation 1′, because

$$y = h,\ a = \sqrt{\frac{T}{d}},\ \text{and } W_1 = \theta.$$

The above is a second method for calculating the angles W_1 and O_1.

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[7] Coghill, Will H., and Anderson, C. O., On the molecular physics of ore flotation: Jour. Phys. Chem., vol. 22, Apr., 1918, p. 244.

To obtain the value of the angle O_2 from the equilibrium of the lower surface of the oil lens requires a consideration of the two heads of liquid acting. As in the equilibrium of the water surface, the force acting to the right is the interfacial tension, $T_{w,o}$, and those acting to the left are the horizontal component of this tension, $T_{w,o} \cos O_2$, and the force (equal to the difference of the liquid heads) restraining the head of liquid. Let this force be *F*. From Figure 3, the force due to the head of water from its surface to the bottom surface of the oil is

$$\left[\left(\frac{y-z}{2}\right)+z\right]\left[y-z\right],$$

and the force due to the head of paraffin oil is

$$\left[\left(\frac{y-z}{2}\right)+x+z\right]\left[y-z\right]\left[0.85\right].$$

Then F, the difference of these two forces, is

$$F=\left\{\left[\left(\frac{y-z}{2}\right)+x+z\right]\left[y-z\right]\left[0.85\right]\right\}-\left\{\left[\left(\frac{y-z}{2}\right)+z\right]\left[y-z\right]\right\}.$$

The equilibrium may then be expressed as

$$F+T_{w,o} \cos O_2=T_{w,o}. \tag{3}$$

For No. 10 in Table 1, this equation becomes

$$\left\{\left[\left(\frac{0.285-0.045}{2}\right)+0.07+0.045\right]\left[0.285-0.045\right]\left[0.85\right]\right\}-$$
$$\left\{\left[\left(\frac{0.285-0.045}{2}\right)+0.045\right]\left[0.285-0.045\right]\right\}+0.0549 \cos O_2=0.0549.$$

Simplifying,

$$0.00834+0.0549 \cos O_2=0.0549,$$

and

$$O_2=31^\circ\ 50'.$$

A comparison of columns 4 and 7 affords an interesting method of determining the consistency of the cathetometer observations recorded in Table 1. Column 6 shows the total thickness of the oil lens, and column 7 shows this thickness multiplied by 0.85, the specific gravity of paraffin oil. Column 4 gives the head of water from its surface to the plane of the bottom of the oil. The head of paraffin oil exceeds the head of water by a small amount, between 0.004 gram weight and 0.016 gram weight. This is natural, because it is known that there is an excess pressure (over the "normal pressure") on the concave side of any liquid surface, and only with lenses of infinite lateral dimensions is the interfacial surface not concave.

These calculations show that the angles determined by the equilibrium triangle are checked within a small percentage of error. Thus the angles for a paraffin lens on water, as obtained by actual measurement, are approximately the same as those obtained by substituting experimentally determined surface tensions in the cosine formula.

CARBON TETRACHLORIDE, WATER, AND AIR.

The next step in this study was to make observations on a system consisting of carbon tetrachloride, water, and air. A diagram of a water globule floating on carbon tetrachloride is shown in Figure 5.

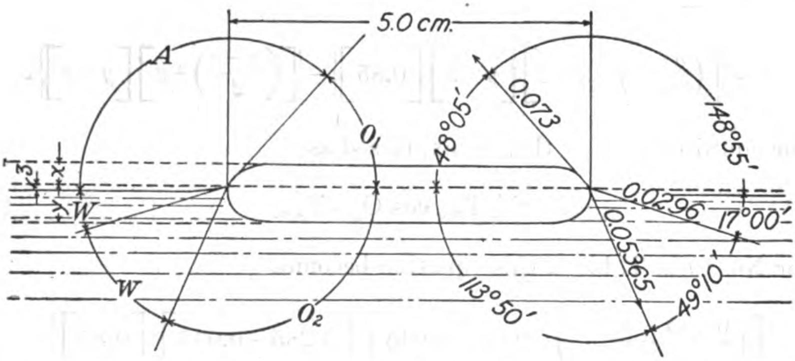

FIGURE 5.—Vertical section of a globule of water floating on carbon tetrachloride; dimensions shown in Table 2. Natural size.

Preliminary tests revealed that water floats on carbon tetrachloride as a flattened globule much rounded at its edge. This group of fluids has some characteristics different from that of the paraffin oil, water, and air. The water globule has a greater tension than either of those of the other interfaces; hence, the so-called "oil angle" is large, whereas it is small in the first system studied. Also, the thickness of the water lens is much greater than that of the paraffin oil. This seems natural because of the greater difference in specific gravities (0.60 as compared with 0.15). The meniscus of the carbon tetrachloride liquid turns upward to meet the surface of the water globule. This fact and the fact that the oil angle is obtuse are why the so-called water or liquid angle is acute.

TABLE 2.—*Calculated values of the air, oil, and water angles, A, O, and W, respectively, from cathetometer observations on a water globule on carbon tetrachloride.*

Carbon tetrachloride has sp. gr. 1.60 and is very slightly soluble in water.

(By equilibrium triangle, $A=143° 00'$, $O=161° 30'$, and $W=55° 30'$, when the sides are $T_{o,a}=0.073$, $T_{w,a}=0.0296$, and $T_{w,o}=0.05365$ gram per cm.)

Volume of globule.	Vertical dimensions.				Diameter of globule.	A	O	W	O_1	O_2	W_1
	x	y	z	$x+y$							
C.c.	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*
12.00	0.295	0.490	0.075	0.785	5.0	148 55	190 45	20 20	48 05	142 40	17 00

TABLE 3.—*Calculated values of the air, oil, and water angles A, O, and W, respectively, from cathetometer observations on paraffin oil lens floating on soap solution (sp. gr. 1.00).*

(By equilibrium triangle, $A=144° 30'$. $O=55° 50'$. and $W=159° 40'$ where the sides are $T_{o,a}=0.0301$, $T_{w,a}=0.0714$, and $T_{w,o}=0.05009$ gram per cm.)

Test No.	Volume of lens.	Vertical dimensions.				Diameter of lens.	A	O	W	O_1	O_2	W_1
		x	y	z	$x+y$							
	C.c.	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*
1	3.00	0.075	0.445	0.020	0.52	4.25	144 00	72 40	143 20	31 40	41 00	4 20
2	3.60	.085	.415	.025	.50	4.45	137 50	82 40	139 30	36 50	45 50	5 20

OBSERVATIONS.

The tensions, in grams per centimeter, as determined by the drop-weight method are: $T_{o,a}=0.073$; $T_{w,a}=0.0296$; $T_{w,o}=0.05365$.

By use of the cosine formula, the following values for the corresponding angles of the force triangle were obtained: $W=55° 30'$; $O=161° 30'$; and $A=143° 00'$.

RESULTS.

The results of the cathetometer observations on this system are shown in Table 2. The observations were made in as short a time as possible, because carbon tetrachloride is slightly soluble in water. In this system the "oil angle" is the one that includes the water globule, and the "water angle" is the one that includes the body of carbon tetrachloride. The air angle calculated from these measurements checks closely the air angle calculated by the equilibrium triangle method, but the other angles do not check so well. The total thickness ($x+y=0.785$) of the water globule multiplied by $\frac{100}{160}$ slightly exceeds the head of carbon tetrachloride. This result is consistent with the observations of paraffin oil on water, and lends confidence in the accuracy of the observations. The distinction should be made that the agreement is best where the calculations involve the surface-tension forces rather than those of the dineric interface.

MODIFIED SOLUTIONS—AQUEOUS SODIUM OLEATE, PARAFFIN OIL, AND AIR.

Next, study was made of the equilibrium of two liquids and a gas; one of the liquids, as water, was modified by a substance such as soap or acetic acid.

Pure, acid free, sodium oleate was added to distilled water. Both the surface tension of the water, and the interfacial tension of the oil against the water was thus modified. Care was taken in modifying the water with soap that the three tensions resulting would have such a relation that no one of them would be greater than the sum of the other two; or in other words the force triangle would be real, and one fluid would not spread over the interface of the other two. How this can be predicted is shown in the discussion following the presentation of the experimental results.

By using a dilute soap solution the tensions in grams per centimeter, as obtained by the drop-weight procedure, were: $T_{o,a}=0.0301$; $T_{w,a}=0.0714$; and $T_{w,o}=0.05009$.

An equilibrium triangle can be constructed with these values as its sides. The angles obtained by the cosine formula are: $A=144°\ 30'$; $O=55°\ 50'$; and $W=159°\ 40'$.

Cathetometer observations on paraffin lenses floating on soap solution were made and the results collected in Table 3. The angles A, O, and W were calculated from the cathetometer observations as in the case of paraffin oil on pure water.

It should be noted that the calculated values of all of these angles do not check closely with the corresponding values obtained from the equilibrium triangle. The air angle checks with the equilibrium-triangle value, but the oil and water angles do not check with their respective equilibrium-triangle values.

AQUEOUS SODIUM OLEATE, BENZENE, AND AIR.

Experimental work on lenses of pure benzene (C_6H_6) on soap solution followed. Benzene (specific gravity 0.88) spreads on pure water, but does not on certain soap solutions. An 0.01 per cent sodium oleate solution was chosen. The tensions, as determined in grams per centimeter, are: $T_{o,a}=0.0296$; $T_{w,a}=0.0558$; and $T_{w,o}=0.0331$.

Benzene corresponds to the paraffin oil in the preceding experiments. The angles of the force triangle of the tensions are: $A=150°\ 50'$; $O=54°\ 40'$; and $W=154°\ 30'$.

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The results of the cathetometer observations on this system are shown in Table 4. The angles A, O, and W were obtained as in previous calculations. The air angle checks with that obtained by the triangle method, but the water angle is larger and the oil angle smaller than the corresponding angles of the triangle. These differences seem to accord with the fact that the lens spreads slowly and flattens out. This slow spreading also indicates a decrease in the interfacial tension as adsorption proceeds with the passage of time. Therefore, in order to gain further information on these points, a close study was made of paraffin lenses on solutions of acetic acid in water.

AQUEOUS ACETIC ACID, PARAFFIN OIL, AND AIR.

Glacial acetic acid (99 per cent) was used in making an aqueous solution of approximately 10 per cent strength; this solution had a specific gravity of 1.016. The interfacial-tension test was performed by dropping the acid solution into paraffin oil. The reverse procedure could not be followed (by use of a brass tip) because the acid displaces the oil upon tip.

TABLE 4.—*Calculated values of the air, oil, and water angles A, O, and W, respectively, from cathetometer observations on a benzene lens floating on aqueous soap solution (0.01 per cent).*

(By equilibrium triangle, $A = 150° 50'$, $O = 54° 40'$, and $W = 154° 30'$, where the sides are $T_{o,a} = 0.0296$, $T_{w,a} = 0.558$, and $T_{w,o} = 0.0331$ gram per cm.)

Volume of lens.	Vertical dimensions.				Diameter of lens.	A	O	W	O_1	O_2	W_1
	x	y	z	$x+y$							
C. c.	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*
1.10	0.025	0.215	0.030	0.240	3.03	....	....	....	....	....	....
1.55	.025	.210	.035	.235	3.68	....	....	....	....	....	....
2.25	.030	.230	.035	.260	4.30	151 10	40 10	168 40	20 20	19 50	8 30

TABLE 5.—*Calculated values of the air, oil, and water angles A, O, and W, respectively, from cathetometer observations on a paraffin lens (2.90 c. c. in volume) on 10 per cent acetic acid solution (sp. gr. 1.016) at intervals for a period of time.*

(By equilibrium triangle, $A=140° 38'$, $O=70° 07'$, and $W=149° 15'$, where the sides are $T_{o,a}=0.0301$, $T_{w,a}=0.0553$, and $T_{w,o}=0.03735$ gram per cm.)

Time.	Vertical dimensions.				Diameter of lens.	A	O	W	O_1	O_2	W_1
	x	y	z	$x+y$							
Min.	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Cm.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*	*Deg. min.*
10	0.040	0.185	0.020	0.225	4.60	156 48	41 26	161 06	18 16	23 10	4 56
65	.040	.180	.020	.220	5.10	156 48	....	....	18 16	....	4 56
110	.040	.160	.020	.200	5.40	156 48	....	....	18 16	....	4 56
185	.030	.140	.020	.170	5.60	159 50	....	....	15 14	....	4 56
290	.020	.130	.015	.150	6.00	165 58	21 32	172 30	10 22	11 10	3 40

The tensions, in gram per centimeter as determined by the drop-weight method, are: $T_{o,a}=0.0301$; $T_{w,a}=0.0553$; and $T_{w,o}=0.03735$.

The angles between the tensions as calculated by the cosine formula are: $A=140° 38'$; $O=70° 07'$; and $W=149° 15'$.

OBSERVATIONS.

Cathetometer observations of a large lens of paraffin oil floating on the acid solution were made periodically for several hours, in order to watch the spreading, or flattening, of the lens. After about five hours the diameter of the lens had increased 30 per cent over its original value. (See Table 5.) In none of the observations at the different intervals of time do the values of the angles, A, O, and W, check closely with those of the force diagram. The oil angle, O, varies from 41° 26′ to 21° 32′, but at all times is less than the force-triangle value, 70° 07′.

The decrease in the value of O correlates with the fact that the lens slowly spreads. This indicates that the figure for the interfacial tension, 0.03735, used in calculating was too large; or, in other words, along the interface of the paraffin oil and the water-acid solution, a change—namely, adsorption—takes place which decreases the value of the tension along the common surface and causes the lens to flatten. Thus, if a value for the water-oil tension, $T_{w,o}$ smaller than 0.03735 were used as one side of the force diagram, the resultant oil angle obtained would be more in accord with that calculated from cathetometer observations.

In order to determine whether a measurable change actually takes place along the interface, some slow drop-weight tests were made, the element of time being the important factor considered. Very slow dropping of the acetic acid solution (1 drop each 10 minutes) into paraffin oil gave a tension not appreciably different from that determined by a faster rate of dropping.

Apparently a drop of acetic acid solution submerged in paraffin oil does not present the same conditions favoring adsorption as a lens of paraffin oil on the surface of the acid solution. An attempt was made to approach these latter conditions in the drop-weight test by reversing the method of dropping so as to expose to the acid solution a drop of paraffin oil as it was forming. Paraffin oil was dropped upward from the inside edge of a hollow glass tip placed in the acid solution. The oil hinged on the inner edge of the tip because the solution replaced the oil on the glass. The use of a very slow rate of dropping gave opportunity for adsorption at the interface. The resultant tension, 0.034 gram per cm., was lower than the tension, 0.03735 gram per cm., as determined by a faster rate of dropping that allowed for less time for adsorption or any other change (as chemical solution) to take place.

The above experiment indicates at least two things: (1) A gradual change takes place along the interface when a lens of a liquid is resting upon the surface of a modified liquid. (2) In drop-weight determinations, the time factor and the order of dropping—that is, whether the dropping liquid is the pure or modified one—are highly important when adsorption plays a prominent rôle.

Review of the results obtained in this experimental work on systems where one liquid was modified shows that in none of the three systems tried do the angles determined by cathetometer observation check closely with those calculated for the force triangle by the cosine formula. However, the writers believe that the angles obtained by the latter method are the same as the corresponding angles that exist between the tensions when one liquid is *first* superimposed upon another, or at least at the instant of superimposing. These angles change, though, as changes along the interface progress. Therefore, it can not be predicted from drop-weight determinations what the exact value of the angles between the tensions will be when a lens of one liquid lies superimposed upon another liquid, one of which is modified.

APPLICATION OF THE NEUMANN TRIANGLE.

Neumann's method of graphic analysis may be applied exactly to the immiscible liquids and qualitatively to the miscible liquids in Table 6, which contains data obtained by Harkins, Brown, and Davies.[8] The table contains the data for the interfacial tensions which have thus far been determined, together with the values of the surface tensions of the pure liquids. All tensions were determined either by the drop-weight method as standardized by Harkins and his colleagues, or from other workers' data to which corrections determined by them have been applied. The tension of water is taken to be 72.80 dynes per centimeter.

In this table are two columns not found in the original articles. One of these is the column headed "difference," which gives the difference between the tensions of the respective liquids and the tension of pure water at the temperature stated. The other added column is headed "specific gravity." The solubilities of the given liquids in water range from practical immiscibility to partial miscibility. Regarding this property, the original workers say:

> In making up this table, in order to make it as general as possible, some acids and alcohols which are very soluble in water have been included.

This means that the interfacial tension is not that of pure liquids, but of one liquid modified by another, or of mutually modified liquids. Solubility is followed by adsorption, which tends to obliterate the interface and to reduce interfacial tension, so that the tension approaches zero as a minimum.

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[8] Harkins, W. D., Brown, F. E., and Davies, E. C. H., The structure of the surfaces of liquids, and solubility as related to the work done by the attraction of two liquid surfaces as they approach each other: Jour. Amer. Chem. Soc., vol. 39, 1917, p. 354.

TABLE 6.—*Data on the surface tensions of 37 liquids, their interfacial tensions against water, and the difference between their surface tensions and that of water.*

Liquid.	Temperature, °C.	Surface tension, dynes per cm.	Interfacial tension, dynes per cm.	Difference, dynes per cm.	Specific gravity.
	Interfacial tension less than "difference."				
Isopentane	20.0	13.72	49.64	59.08	0.626
Hexane	25.0	18.71	49.54	53.34	.663
Octane	20.0	21.77	48.61	51.03	.706
Octylene	17.0	22.33	22.66	50.90	.722
Trimethyl ethylene	20.0	17.26	36.69	55.54	....
Chloroform	20.0	27.30	27.70	45.50	1.526
Ethyl iodide	16.0	29.85	40.02	43.53	1.944
Methyl alcohol	20.0	22.70	0.82	50.10	.789
Isobutyl alcohol	18.0	23.00	1.76	50.09	.803
Isoamyl alcohol	20.0	24.10	4.42	48.70	.825
Octyl alcohol	20.0	27.49	8.52	45.31	.837
Cyclohexanol	16.2	34.23	3.92	39.12	.962
Mercaptan	20.0	21.82	26.12	50.98	.835
Ethyl ether	20.0	17.10	10.70	55.70	.718
Isovaleric acid	20.0	25.33	2.73	47.47	.955
Capryllic acid	18.1	28.82	8.22	44.25	.918
Oleic acid	20.0	32.27	16.05	40.53	.708
Ethyl capronate	20.0	25.81	25.46	46.99	.870
Ethyl nonolate	20.0	28.04	23.88	44.76	....
Ethyl carbonate	20.0	26.31	12.86	46.49	.978
Castor oil	17.0	37.14	22.63	36.09	.950
Benzene	20.0	28.98	34.97	43.82	.880
Toluene	25.0	27.70	36.10	44.35	.882
M-xylene	25.0	28.30	37.60	43.75	.878
Ethyl benzene	17.5	29.62	31.15	43.54	.867
Styrene	19.0	32.14	35.48	40.79	.912
P-cymene	13.5	28.75	39.41	45.01	.855
Benzyl alcohol	22.5	39.71	4.75	32.71	1.023
Dimethyl aniline	25.0	36.02	25.78	36.03	.955
Ethyl phthalate	20.5	37.34	16.27	35.39	1.126
Ethyl cinnamate	19.5	38.42	21.36	34.45	1.066
Ethyl hydrocinnamate	21.5	35.08	20.19	37.49	1.012
	Interfacial tension greater than "difference,"				
Carbon bisulphide	16.0	33.52	54.09	39.86	1.259
Cyclohexane	16.8	25.80	60.60	47.46	.779
Oil C, higher paraffins	17.0	31.81	57.25	41.42	.850
Carbon tetrachloride	17.0	27.59	52.63	45.64	1.608
Benzene iodide	16.8	40.35	45.67	32.91	1.733

The meaning of the figures in Table 6 may be interpreted further. The liquids have been divided under two heads—those giving with water an interfacial tension less than the "difference," and those giving an interfacial tension greater than the "difference." The liquids from isopentane to ethyl hydrocinnamate have interfacial tensions against water which are less than the difference between the surface tension of water and that of the liquid. Thus the surface tension of water (72.80) minus the surface tension of isopentane (13.72) equals 59.08, which is greater than the interfacial tension of isopentane against water (49.64). This shows that for isopentane, water, and air the equilibrium triangle of forces is imaginary, because one force—the surface tension of water—is greater than the sum of the other two forces; also, that isopentane placed on water will spread and form a film. (The application of the force triangle must be made when one liquid is first superimposed upon another; as time passes, various changes may take place.) In such a system there is an unbalanced resultant force acting in the direction of the surface tension of the water and tending to spread the isopentane out in as thin a layer as possible over the surface of the water. This condition holds true for all of the other liquids mentioned in the upper part of the table.

Most of these liquids have a specific gravity less than water, consequently do not sink in water. With liquids of a greater specific gravity than water a mistake may be made such as is found in Barker's[9] textbook, where he says:

> In illustration of these actions, let the three fluids be water, oil, and air. The water-air tension is as above, 81 dynes, the air-oil tension, 36.88 dynes, and the water-oil tension is 20.56 dynes. The sum of the last two is 57.44; very considerably less than the water-air tension above. Hence, a drop of oil on the surface of water can not be in equilibrium. The superior tension of the water film draws it out indefinitely, until it becomes so thin as to lose entirely the properties of a liquid mass. Conversely, if a drop of water be placed on chloroform, the water-air surface tension being greater than the sum of the chloroform-air and the chloroform-water tensions—that is, 81 > (29.53+30.61)—the water gathers itself at once into a drop.

The reasoning of the latter part of this quotation is incorrect because no equilibrium of forces is possible when one force is greater than the sum of the other two, no matter which is the superimposed liquid. What actually happens, as regards water on chloroform, is that the water forms a flattened globule in the surface of the chloroform; the chloroform spreads over the surface of the globule. The water globule rides in the surface with about 65 per cent of its depth submerged in accordance with Archimedes' principle of buoyancy. The surface tension of the chloroform exerts a slight effect in pulling down the globule of water. These statements are supported by the writers' cathetometer measurements of water globules on chloroform.

Under the second heading of the table are found five liquids whose interfacial tension against water is greater than the difference between the surface tension of water and that of the liquid. Thus the tension of water (72.80) less the tension of carbon tetrachloride (27.59) is not greater than the interfacial tension (52.63). In this system no tension is greater than the sum of the other two and a triangle of forces is possible and real. Water will form a globule on the surface of carbon tetrachloride (specific gravity 1.60), as shown in Figure 5. The diagram represents the conditions observed, by means of a cathetometer, in the writers' study.

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[9] **Barker, G. F., A textbook of physics, 1892, pp. 206–207.**

The triangle is also real when any one of the other four liquids is in contact with water. Thus cyclohexane and oil C (higher paraffins) will form lenses on the surface of water and will not spread out over the surface in a thin film. Water will form a lens (better called a flattened globule) on carbon bisulphide, carbon tetrachloride, and benzene iodide.

FLOATING OF HEAVY LIQUIDS ON LIGHTER LIQUIDS.

In the above-mentioned tests the lighter liquid was superimposed upon the heavier one. An interesting phenomenon is that very small drops of water may be floated by film suspension in cyclohexane and in paraffin oil. Also small drops of carbon bisulphide or carbon tetrachloride may be floated in the same manner in water. This flotation of a heavier liquid by a lighter one by surface-tension effect is analogous to the floating of sulphides on water. In Figure 6, sketch A shows a small drop of carbon tetrachloride and B a particle of galena, both floating on water by film suspension. These sketches represent the conditions as observed in actual tests.[10]

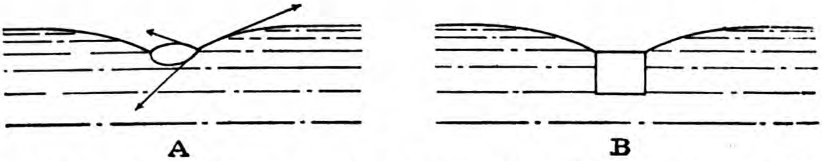

FIGURE 6.—Observed analogous floating of carbon tetrachloride (sp. gr. 1.60) and galena (sp. gr. 7.5) on water.

Rayleigh offered an explanation for the failure of carbon bisulphide to spread on water. He stated that a lens of carbon bisulphide on water evaporates so rapidly at its edge that it spreads only a short distance. The writers observed a different conduct. Carbon bisulphide (specific gravity, 1.259) when placed on water sank, except when very small drops were used; then the drop formed into a flattened globule and floated in the surface by film suspension.

Although the Neumann triangle does not predict the absolute values of the angles existing between the planes of the tensions for the case of two liquids in contact, one of them being modified, the inequalities represented by the triangle do serve as a basis for predicting whether or not one liquid will spread upon another when they are first placed in contact. As may be noted in the experimental work, a liquid may first form a lens upon a second liquid, and later with the passage of time approach the condition of a spreading liquid.

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[10] Cyclohexane and benzene iodide were not available for the tests.

TABLE 7.—*Behavior of benzene and aqueous soap solution when superimposed one upon the other.*

1	2	3	4	5	6	7		
No.	Strength of solution (per cent).	$T_{w,a}$ soap solution, air (dynes per cm.).	$T_{o,a}$ benzene, air (dynes per cm.).	$T_{w,o}$ soap solution, benzene (dynes per cm.).	Triangle of forces.	Inequalities.	Behavior of liquids.	
							Benzene superimposed.	Aqueous solution superimposed.
1	0.0000	73	29	35	Imaginary.	$T_{w,a} > T_{o,a} + T_{w,o}$	Spreads	Sinks.
2	.0012	68	29	34.7	...do	$T_{w,a} > T_{o,a} + T_{w,o}$	...do	Do.
3	.0025	63	29	34.5	Real	$T_{w,a} > T_{o,a}$; $T_{w,o} > T_{w,a} - T_{o,a}$	Forms lens and floats.	Forms globule and floats.
4	.0100	49	29	33	...do	$T_{w,a} > T_{o,a}$; $T_{w,o} > T_{w,a} - T_{o,a}$.	...do	Do.
5	.0300	34	29	23	...do	$T_{w,a} > T_{o,a}$; $T_{w,o} > T_{w,a} - T_{o,a}$.	...do	Do.
6	.0600	24	29	14	...do	$T_{o,a} > T_{w,a}$; $T_{w,o} > T_{o,a} - T_{w,a}$.	Forms flattened globule and floats.	Do.
7	.4000	25	29	3	Imaginary.	$T_{o,a} > T_{w,a} + T_{w,o}$	Floats by buoyancy.	Spreads.

BENZENE AND VARIOUS AQUEOUS SODIUM OLEATE SOLUTIONS.

The results of a study in the spreading of liquids by experiments with benzene and various aqueous soap solutions are tabulated in Table 7. Chemically pure benzene and acid-free sodium oleate in distilled water were used. The tensions were determined by the drop-weight method. The diagram of forces applied to these experimentally determined tensions was found to predict the deportment of the liquids in contact with each other.

In series 1 and 2 in the table the tension of the pure water or of the soap solution used exceeds the sum of the benzene tension and the interfacial tension. The triangle of forces is therefore not real, but imaginary, and the liquid with the weaker tension (the benzene) spreads over the surface of the liquid with the stronger tension (the water or the soap solution) provided the lighter liquid is superimposed upon the heavier one. If either the pure water or the soap solution used in the second series is placed upon the benzene surface, the benzene immediately spreads over the heavier liquid, pulling it down and permitting it to sink.

For series 3, 4, 5, and 6, the tension of the soap solutions used is less than the sum of the benzene tension plus the interfacial tension. In these combinations no one force is greater than the sum of the other two, and the force triangle is possible and real. In series 3, 4, and 5, when benzene is placed upon the soap solution, the benzene forms a lens, as in the system of paraffin oil on distilled water; the

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oil angle is acute. The oil angle will always be acute when the soap solution tension, $T_{w,a}$ exceeds the benzene tension, $T_{o,a}$. In series 6, however, $T_{o,a}$ exceeds $T_{w,a}$; hence the oil angle is obtuse, as with water on carbon tetrachloride, and the benzene forms a flattened globule on the surface. A small quantity of the soap solution when placed upon the benzene draws into a tiny globule that is nearly spherical and floats by film suspension in a manner analogous to sulphides on water.

No. 7 represents a set of conditions different from those just considered. The tension of the benzene exceeds that of the soap solution and also exceeds the sum of this latter tension and the interfacial tension. The force diagram is imaginary; the soap solution, having the weaker tension, spreads over the benzene surface; this is the reverse of what happened in Nos. 1 and 2. The benzene, therefore, forms a globule in the surface of the soap solution and floats by buoyancy like water on the surface of chloroform. A small quantity of soap solution of this strength placed upon benzene will spread and not sink, although it has the greater specific gravity.

This table further shows that the force diagram passes from "imaginary" limits through a "real" range and again into imaginary dimensions as the strength of the soap solution is increased. Thus a spreading tendency exists at widely different concentrations of soap solution and nonspreading in the intermediate range. In Nos. 1 and 2 the ability to spread is accompanied by a relatively high interfacial tension, 35 and 34.7 dynes per centimeter; in these tests this property seems to be purely a physical manifestation. In No. 7 it is accompanied by a very small interfacial tension, 3 dynes. Low interfacial tension for two pure liquids indicates solubility, but for modified liquids it represents, according to one of the accepted theories of emulsification, a good condition for emulsification. An emulsion of benzene in soap solution does occur when this low interfacial tension exists. Accordingly, the property of spreading with low interfacial tension is not only a physical one, but is aided by the tendency to form an emulsion.

Thus the application of Neumann's triangle gives much information as to spreading and nonspreading of liquids, and may even aid in the knowledge of emulsions.

PARAFFIN OIL AND VARIOUS AQUEOUS SODIUM OLEATE SOLUTIONS.

With reference to Table 6, a few comments may be made on the deportment of paraffin oil on various strengths of aqueous soap solutions. The surface tension of pure water is 72.80 dynes per centimeter, and the interfacial tension against paraffin oil is 57.25. Soap added to the water reduced these tensions in an approximately proportionate ratio. Thus a spreading solution would not be expected until the surface tension of the solution reached 24 or 25 dynes (the lowest limit to which water tension can be depressed by the addition of soap) and the interfacial tension about 5 or 6 dynes. Then the surface tension of the paraffin oil is greater ($31.81>24+5$) and a spreading solution would result. The soap solution would spread upon the paraffin oil, but, under no circumstances, would the oil be expected to spread on any soap solution. With paraffin oil and soap solution, a spreading liquid is obtained only with low interfacial tension. Also spreading is not present in two widely different ranges of concentration, as in benzene and soap solutions. By analogy this latter statement applies to the deportment of any of the five liquids (under the second part of Table 6) in contact with modified water.

The experiments where aqueous solutions were used give some evidence for the following generalizations. When the liquids given under the first part of Table 6 (excluding those very soluble in water) are brought in contact with water modified by a substance, such as soap, two types of spreading may occur: (1) Spreading accompanied by a relatively high interfacial tension when the liquid spreads over the surface of the soap solution (a high interfacial tension opposes the formation of emulsions); and (2) spreading accompanied by a low interfacial tension when the soap solution spreads over the given liquid. The intermediate range indicates where neither liquid spreads over the other, and the Neumann triangle is real. The low interfacial tension is a condition regarded by scientists as conductive to the formation of an emulsion in which soap solution is the continuous phase.

When the liquids given under the second part of Table 6 are brought in contact with solutions of soap and water, spreading does not take place except when the interfacial tension is low; then the soap solution always spreads over the given liquid. When the interfacial tension is not low, the Neumann triangle is real and no spreadability of liquids results.

A knowledge of the Neumann triangle should be regarded as fundamental to the student of flotation principles. When an oil is added to an aqueous solution, it will spread over the surface of the solution, provided the following inequality is true:

$$T_{w,a}>T_{o,a}+T_{w,o}.$$

If some substance is added to the solution which lowers $T_{w,a}$ but does not lower $T_{o,a}+T_{w,o}$ by an equal proportion, the inequality is reduced and may reach a point where the oil will not spread upon the solution. Such an instance is noted with the soap solutions discussed. This may be the reason why soap, saponin, and other substances that tend to change the inequality mentioned have a deleterious effect in flotation when used in excess.

The surface tension of the oil is not changed appreciably by adding inorganic salts to a flotation solution. This fact offers the suggestion that substances may be found that have no effect on the tensions of water and of oil, but do reduce the interfacial tension. Such a state of affairs would result in an augmented inequality, giving the worker a greater margin when he desires to obtain a spreading condition. Alkalies and, for some oils, acids have been found to have this effect.[11] To be sure, it must be remembered that there is the possibility of saponification when alkali is in the presence of oil. If this results, the oil is no longer an oil but another product. Adding an alkali may sometimes defeat the purpose of the addition.

SUMMARY.

The work represented in this paper may be summarized as follows: The Neumann equilibrium triangle was employed jointly with cathetometer observations of a lens of one liquid resting on another. The angles derived by the use of the Neumann triangle and those derived by principles of mechanics have been compared.

The configuration of the surfaces and the interface of a lens of one liquid resting on another has been shown in detail by drawings.

The following combinations were studied—paraffin oil on water, carbon tetrachloride on water, aqueous sodium oleate and benzene, aqueous acetic acid, and paraffin oil.

Of all the combinations mentioned paraffin oil and water would be expected to show a minimum adsorption. Here the observed angles check closely the Neumann triangle values of these angles. In the other combinations the " air " angles check, but the other two angles—where the observed values for the interfacial tensions are employed—show marked disagreement with the Neumann triangle values of the angles. The disagreement can probably be attributed to a failure to make the interfacial tension tests under conditions similar to those where the cathetometer readings were observed.

The analogy of the flotation of a heavy liquid and of a solid, each floating by " film suspension," has been discussed.

By the system of reasoning employed throughout the paper the prediction was made that the strengths of soap solutions could be modified so that small globules of them would float by " film suspension " on benzene (sp. gr. 0.88) and on paraffin oil (sp. gr. 0.85). Small globules of soap solution were then floated on the abovementioned liquids.

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[11] Corliss, H. P., and Perkins, C. L., The theory of ore flotation: Jour. Ind. and Eng. Chem., vol. 9, 1917, p. 484.

PART II.—SURFACE-TENSION PHENOMENA OF A SOLID, A LIQUID, AND A GAS IN CONTACT; THE ANGLE OF CONTACT AND THE EDGE EFFECT.

INTRODUCTION.

Part 1 of this paper discusses the equilibrium of the interfacial-tension forces of two liquids and a gas in contact. The discussion that follows bears on the equilibrium and other surface-tension phenomena when one of the liquids is replaced by a solid—that is, when one gaseous, one liquid, and one solid substance are in contact.

TENSIONS AT THE CONTACT OF THREE SUBSTANCES WHEN ONE IS A SOLID.

In studying three fluids in contact, one has to deal with mobile substances and with three tensions acting at various angles to each other. When a constraint is put on such a system, a readjustment of the equilibrium conditions within the system readily takes place by changes of the tensions and usually results in changes of the angles between the tensions. When one of the liquids is replaced by a solid, the problem becomes more difficult.

When a solid, liquid, and a gas in equilibrium have a common meeting line, two of the tensions or interfacial forces must, under any conditions, act in opposite directions at right angles to this line—that is, tangentially to the solid. The idea of a stretched film exerting a distinct tension at the surface of a solid is not readily conceived when considering the equilibrium of a line of contact of two fluids and a solid. Rayleigh[1] states in this connection:

> I find some difficulty in forming a definite conception of superficial tension as applied to the interface of a solid and a liquid. It would seem that the interfacial tension can only be employed in such cases as the immediate representative of interfacial energy.

DIFFICULTY IN DEALING WITH A SOLID, A LIQUID, AND A GAS IN CONTACT.

The principal drawback in considering systems of this kind is the inability to measure the surface energy of a solid. Willows and Hatschek[2] mention a method of limited application for obtaining the tension at the interface of a solid and a liquid. From considerations, both theoretical and experimental, the conclusion has often been drawn that the interfacial energies of solid substances against gases or liquids have a high value as compared with those of liquids and gases. Interfacial energies of liquids (with the exception of mercury) at ordinary temperatures are less than 100 ergs per square centimeter, but undoubtedly the surface energies of solids are much higher. Experimental verification of this statement is, of course, lacking, but will probably result from the work of some of the many investigators on the surface structure of substances.

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[1] Rayleigh, On the theory of surface forces: Phil. Mag. ser. 5, vol. 30, 1890, p. 467.

[2] Willows, R. S., and Hatschek, E., Surface tension and surface energy, 1915, pp. 23–24.

COORDINATION OF SURFACE ENERGY AND SURFACE TENSION.

Poynting and Thomson[3] coordinate the surface energy of a solid with the surface tension of a liquid, and prepare the way for gaining a concept of the angle of contact of a liquid against a solid.

> A solid and two liquid surfaces can be in equilibrium; this is shown by the equilibrium of water or of mercury in glass tubes when we have two liquids, water or mercury and air, both in contact with the glass. The consideration of the condition of equilibrium in this case naturally suggests the question as to whether there is anything corresponding to surface tension at the surface of separation of two substances, one of which is a solid. Though in this case the idea of a skin in a state of tension is not so easily conceivable as for a liquid, yet there is another way of regarding surface tension which is as readily applicable to a solid as to a liquid. We have seen that the existence of surface tension implies the possession by each unit area of the liquid of an amount of potential energy numerically equal to the surface tension; we may from this point of view regard surface tension as surface energy. There is no difficulty in conceiving that part of the energy of a solid body may be proportional to its surface, and that in this sense the body has a surface tension, this tension being measured by the energy per unit area of the surface.

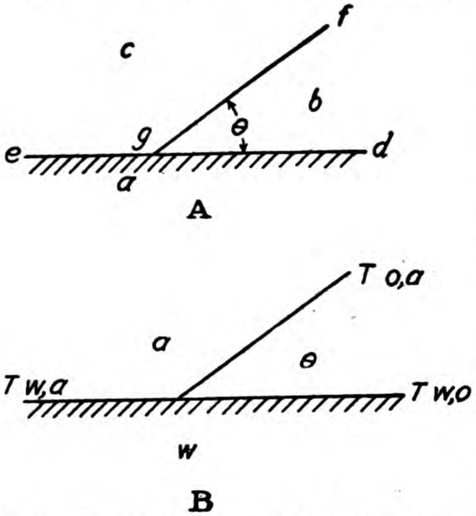

FIGURE 7.—Angle of contact of a liquid against a solid.

> Let us now consider the equilibrium of a liquid in contact with air and both resting on a solid and not acted upon by any forces except those due to surface tension. Suppose *a*, in diagram A, Figure 7, represents the solid, *b* the liquid, *c* the air, *f g* the surface of separation of liquid and air, *e d* the surface of the solid; let the angle *f g d* be denoted by *θ*; this angle is called the angle of contact of the liquid with the solid.

EQUATION FOR THE CONTACT ANGLE.

DERIVATION.

An equilibrium equation for the contact angle can be readily expressed. In diagram B, Figure 7, let *w* represent the solid, *o*, the liquid, and *a*, the gas; then let $T_{w,a}$, $T_{o,a}$, and $T_{w,o}$ be the immediate representatives of interfacial energies.[4] Evidently when the system is in equilibrium under any given conditions the following expression is true:

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[3] Poynting, J. H., and Thomson, J. J., A textbook of physics, 1902, p. 139.

$$T_{w,a} = T_{w,o} + T_{o,a} \cos \theta,$$

and, by transposition. $$\cos \theta = \frac{T_{w,a} - T_{w,o}}{T_{o,a}} \qquad (1)$$

DISCUSSION.

The equation for equilibrium here is determined by a method of projection upon the solid; the equation gives only the equilibrium along one line in the plane of the paper and determines the direction of the liquid-air tension force, whereas the equation for the Neumann equilibrium triangle of interfacial fluid tensions applies to all lines in the plane of the paper, but the force of gravity must be taken into account before the directions of the forces can be determined.

If $T_{w,a}$ is greater than $T_{w,o}$, $\cos \theta$ is positive and the angle of contact is less than a right angle; if $T_{w,a}$ is less than $T_{w,o}$ the cosine is negative, and θ is greater than a right angle.

This formula is introduced not for the purpose of obtaining the value of θ by means of it, but rather because it serves an an aid in discussing the angle. The angle of contact can not be calculated from the equation because the two quantities $T_{w,a}$ and $T_{w,o}$ have not been determined experimentally.

An interesting point to be observed in this expression is that for any finite contact angle the difference of the solid-gas surface tension, $T_{w,a}$, and the solid liquid tension, $T_{w,o}$, must never be greater than the liquid gas tension, $T_{o,a}$. If it were greater, $\cos \theta$ would be greater than unity; such a value is a physical impossibility. From this consideration a limiting maximum value for finite angles of contact is placed upon the difference, $T_{w,a} - T_{w,o}$. If the angle θ were obtained from some of the various methods, $T_{o,a}$ determined, and then the values of these two quantities were substituted in equation (1), a value of the difference, $T_{w,a} - T_{w,o}$, could be obtained.

ANGLE OF CONTACT IN CONTRAST TO NEUMANN TRIANGLE.

The significance of the angle of contact should now be evident. The angle of contact is the angle at which a liquid meets a solid; that is, the angle between the plane of the wetted surface of the solid and a line drawn tangent to the liquid where the three substances—solid, liquid, and gas—meet, and in a plane at right angles to this common meeting line. It is invariable for stated conditions of liquid and solid, and independent of the slope or dip of the solid, and, as far as known, independent of the curvature of the solid surface. The conditions affecting this contact angle are the nature of the gas, liquid, and solid, the physical condition of the solid surface, the temperature, and the fact whether the liquid advances or retreats over the surface of the solid.

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[4] These letters have been chosen to coordinate with the symbols used in Part 1, where *W* represented the liquid, as water; *O*, the superimposed liquid, as oil; and *A*, the air.

In considering the interfacial tensions of three fluids in contact, the equilibrium triangle serves as a basis for predicting the conduct of one liquid when placed upon the surface of a second liquid not completely miscible with it. This method can not be applied to a consideration of a solid, liquid, and gas in contact, because two of the represented tensions are acting in the same straight line, thus making the construction of a triangle of forces impossible. Fortunately, however, use may be made of the angle of contact to predict the conduct of a liquid upon a solid. The limiting values of the contact angles are 0° and 180°. When the angle of contact is 0°, the liquid is said to wet the solid and to be adsorbed by the solid, forming a liquid film on the surface of the latter and displacing the air film.

Summing up the discussion thus far, it may be said that the angle of contact bears the same relation to the interfacial energies of a solid, a liquid, and a gas in contact as the Neumann equilibrium triangle bears to the interfacial tensions (or energies) of two liquids and a gas in contact.

ANGLE OF CONTACT AND FLOATABILITY OF CYLINDRICAL OBJECTS.

In earlier work[5] the writers studied the relation of the angle of contact to the floatability of cylindrical objects and arrived at the general conclusions given below.

EQUILIBRIUM OF A FLOATING CYLINDER.

The upward forces acting on a unit length of a cylinder floating on a liquid, as water (the contact angle of the water against the solid being finite), are three, as follows: (1) The vertical component of the surface tension acting at the line of contact of the water with the cylinder; (2) the hydrostatic pressure of the water; and (3) the force equal to the weight of water displaced by the submerged portion of the cylinder. The pull of gravity upon the cylinder is in vertical equilibrium with these three forces.

RELATION OF ANGLE OF CONTACT TO THE FLOATABILITY OF CYLINDERS.

In the paper mentioned it was shown that there is a definite curvilinear relation between the angle of contact and the maximum radius of floatability. The radius has a maximum value when the angle of contact is 180°; it is zero when the contact angle is zero.

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[5] Coghill, W. H., and Anderson, C. O., On the molecular physics of ore flotation: Jour. Phys. Chem., vol. 22, 1918, p. 237.

The two most important facts to be grasped from the study of floating cylinders are: (1) The angle of contact may have any value greater than zero, and a substance will be floatable providing its radius is small enough. This fact is a direct refutation of the oft-quoted statement in flotation literature that a substance is not floatable unless it possesses an angle of contact greater than 90°. (2) The value of the surface tension is only a very small proportion of the total upward forces acting when a cylinder is floating.

FLOTATION OF PRISMATIC BODIES.

After having studied floating bodies of cylindrical shape, the writers turned to a consideration of floating bodies of other shapes. Few, if any, ore particles have a shape approaching that of a cylinder; hence the flotation of cylindrical bodies is not an exact parallel to the flotation of ore. Ore particles have many and irregular shapes, usually shapes that have a number of surfaces. Hence, this discussion is concerned with bodies having several surfaces as compared to cylindrical bodies having one continuous surface—the ends of the cylinder being disregarded.

The results obtained are the outcome of studying the old and common after-dinner trick known as the "overfilled tumbler."

CONDUCT OF WATER IN AN OVERFILLED TUMBLER.

The familiar behavior of the meniscus of water against glass in a partly filled tumbler was the starting point in this work. The surface of water, as is well known, turns upward at its contact with a glass wall. Many investigators have assumed that the contact angle of water against glass is zero. For a zero angle of contact the height of the meniscus of water against a vertical glass plate at room temperature would be theoretically about 0.38 cm. In a number of experiments with pure water against well-cleaned glass the writers found no instance where the meniscus reached the theoretical height that corresponds to a contact angle of 0°, but the heights measured correspond to contact angles varying from a few degrees to 30°, depending on the condition and nature of the glass.

When more water is added to a partly-filled tumbler, the meniscus is always present, and its height is constant until the tumbler is "level full," when the meniscus disappears. The further addition of water overfills the vessel; the water bulges upward, forming a convex meniscus, which meets the inner edge of the glass wall. The change in the meniscus of the water as filling and overfilling of the tumbler proceeds is shown in Figure 8. If a thick-walled vessel is used, the water, on continued addition, moves across the horizontal surface intervening between the inner and outer edges. At the outer edge the liquid resumes the bulging which was begun at the inner edge. Sketch C, Figure 8, shows the profiles of the liquid as it meets the inner and outer edges of the tumbler. The height of the profile (dotted) meeting the inner edge is not nearly as great as the one meeting the outer edge. Of course, when enough water has been added, the vessel overflows.

The analysis of this apparent change in the contact angle is taken up in the discussion of edge effects (pp. 38 to 43). This conduct of water with glass may be readily observed and studied through a cathetometer or a low-power microscope.

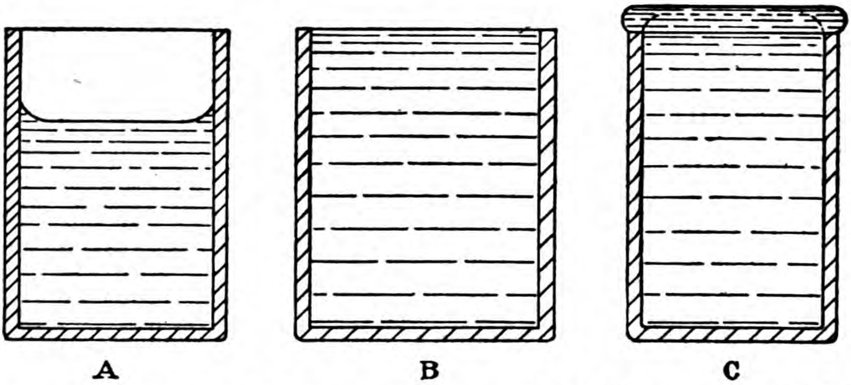

FIGURE 8.—Changes in the appearance of the meniscus as filling and overfilling of a tumbler proceeds.

ONE TUMBLER WITHIN ANOTHER.

A small tumbler was placed within a large one; the smaller one being overfilled with water so that the meniscus turns down to meet the inner edge of the vessel. The larger vessel was filled as indicated in Figure 9. Under such conditions, the liquid in the outer vessel has two menisci; one of these turns downward to the outer edge of the small tumbler, and the other turns upward to the wall of the containing vessel. Apparently, under these conditions, water has two different contact angles against the same substance—glass; if two substances under the same conditions have more than one angle of contact, then the definition of this angle as submitted must be modified.

Two ideas were derived from the examination of the over-filled tumbler: (1) Glass prisms are floatable, and (2) the hinging of the water on the edge of the tumbler presents an anomalous condition. These will be considered in their order.

FLOATABILITY OF GLASS PRISMS PREDICTED.

Attention is called to another feature brought out in Figure 9. If the vessels containing water are viewed from above, the top of the smaller container will appear as an annular glass ring resting or floating in a depression in the water surface. This observation, and the consideration of the hydrostatic head measured vertically between the surface of the water in either vessel and a horizontal plane through the upper surface of the wall of the smaller vessel, led to the belief that small glass prisms were floatable on water.

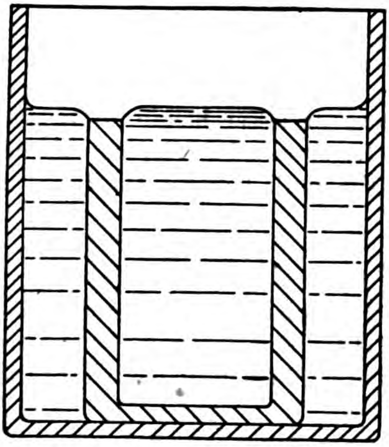

FIGURE 9.—Liquid profiles when a small partly overfilled tumbler is about to be submerged in the liquid in a larger one.

GLASS PRISMS FLOATED.

Small glass prisms about $\frac{1}{16}$ inch square by 2 inches in length were cut from ordinary window glass. Regardless of whether the prisms were cleaned merely by rinsing in distilled water and air-drying, or by thorough scrubbing with a mixture of sulfuric acid and bichromate, they were easily floated, either on distilled water or tap water. The prism was placed in horizontal position on a small pedestal in a glass dish; water was added gently from a burette until the prism was lifted off of the pedestal. Broader and longer pieces were cut and attempts made to float them. It was found that large plate-shaped pieces of thin window glass could be floated.

EDGE EFFECT.

The deportment of the liquid as it passes over the edge of the over-prisms were cleaned merely by rinsing in distilled water and air-filled tumbler may conveniently be called the edge effect. The explanation of this effect removes an anomaly in the study of the angle of contact.

CONSIDERATIONS PROMPTING THE STUDY.

The banking of water along an edge and the apparent inconsistency of the angle of the contact of water with glass prompted a study of the rôle of an edge in the flotation of a body. A further fact that suggested this study was the difference in size of floatable bodies of cylindrical shape and of prismatic shapes or shapes possessing clearly defined edges. The difference in size is quite evident. The largest aluminum cylinder (sp. gr. 2.7) floatable under the best conditions

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has a radius of 0.23 cm., whereas a glass plate (sp. gr. 2.6) of 0.3 cm. thickness is floatable under certain conditions, although it has infinite breadth and length; of course, the cylinder may have infinite length and still be floatable.

The method selected for attacking this problem involved a study of the conduct of liquids at the edges of glass surfaces inclined at various angles to each other. The procedure and the experimental data of these observations are given first; a discussion of the results follows.

PRELIMINARY TESTS WITH PURE WATER.

Preliminary tests proved that greater or lesser heights of water upon a horizontal glass plate could be obtained before the liquid overflowed the side, depending upon the angle between the faces at whose edge the liquid banked.

METHOD.

The general method was to mount a glass plate in a horizontal position, gently add a liquid to the top surface, and determine by means of cathetometer readings the maximum height obtainable before the liquid flowed down the sides of the plate.

GLASS PLATES.

Rectangular plates, about 2 inches square, of heavy plate glass were obtained. The sides of the first plate were carefully beveled so that with one surface the sides made an angle of 20°, and with the other surface an angle of 160°. The second plate was so ground that the respective angles were 30° and 150°. Other plates were ground so that a series of plates were at hand such that the angle between a side and a surface varied by intervals of 10° from 20° to 160°. The exact dimensions of these plates are given in Table 8. The solid angle is that angle between the sides and the top surface of the plate. The surface area given was that of the top surface. Each plate, except No. 8, is, in reality, numbered twice. Thus, the first plate shown in the table is called No. 1 when the solid angle 159° is considered; it is No. 15 when the angle 21° is under discussion. Observations were made on both surfaces of the plate, except for No. 8.

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TABLE 8.—*Dimensions of glass plates used in studying the effect of an edge on the floatability of bodies.*

Plate No.	Length (cm.).	Breadth (cm.).	Solid angle (degrees.)	Area of surface (sq. cm.)
1	2.90	2.75	159	7.97
2	4.23	3.85	146	16.28
3	4.62	4.46	137	20.56
4	4.95	4.87	127	24.10
5	5.20	5.05	117	26.26
6	5.28	5.22	110	27.56
7	5.56	5.40	98	30.02
8	5.65	5.55	90	31.40
9	5.70	5.57	82	31.74
10	5.62	5.60	70	31.47
11	5.67	5.55	63	31.42
12	5.68	5.60	53	31.80
13	5.57	5.43	43	30.24
14	5.63	5.30	34	29.84
15	5.40	5.22	21	28.18

PROCEDURE.

The heights of distilled water on these various plates were first measured. The procedure was as follows: The glass plate was carefully mounted in a horizontal position on a small pedestal. The plates had previously been cleaned in an acid-dichromate mixture and rinsed with alcohol. After air-drying they were rubbed with filter paper and brushed with a camel-hair brush to remove any particles of filter paper or dust. Care was taken not to let the clean plate come in contact with the hand, in order to avoid contamination of the glass surface.

A cathetometer was leveled about 3 feet from the plate and focused on the top surface; this reading was recorded (No. 1). Water was gently added to the surface of the plate from a burette, the outlet of which was about 0.10 cm. above the plate. A reading (No. 2) was taken on the water surface just before the liquid reached the edge of the plate. Another reading (No. 3) was made on the water surface the instant the liquid broke over the edge of the plate.

The difference of the first and second readings gives the height of water from which the angle of contact of the liquid with the glass may be calculated. The difference of the first and third readings gives the maximum liquid height obtainable upon a given plate experimentally. The volume of liquid required to cause overflowing was also noted.

RESULTS OF OBSERVATIONS OF PURE WATER ON GLASS PLATES.

These observations were repeated on each of the series of plates. The experimental results appear in Table 9.

TABLE 9.—*Theoretical and experimental values of the heights, **h**, of distilled water on glass plates with stated solid angles.*

(θ=30°; surface tension, T=0.073 gm. wt. per cm.)

Plate No.	Solid angle (degrees).	Height (h) of liquid.		Volume of liquid (c. c.).
		Theoretical (cm.).	Experimental (cm.).	
	180	0.140	0.140	....
	170	.184	....	....
1	159	.232	.210	1.30
2	146	.286	.255	3.40
3	137	.321	.300	4.50
4	127	.356	.325	5.80
5	117	.391	.355	8.30
6	110	.413	.385	9.00
7	98	.447	.420	10.70
8	90	.467	.460	13.50
9	82	.485	.475	13.50
10	70	.507	.485	13.30
11	63	.518	.500	15.00
12	53	.529	.510	15.30
13	43	.536	.515	15.10
14	34	.539	.530	14.80
15	21	.540	.530	13.80
	10	.540	....	....
	0	.540	....	....

The surface tension of the water and those of the liquids mentioned later were determined by the drop-weight method. The experiments were conducted in a room where the temperature was 20° to 23° C. The densities of the liquids were determined by weighing a known volume.

In this table two general points should be noted: (1) The experimental height increased with a decrease in the solid angle; and (2) it

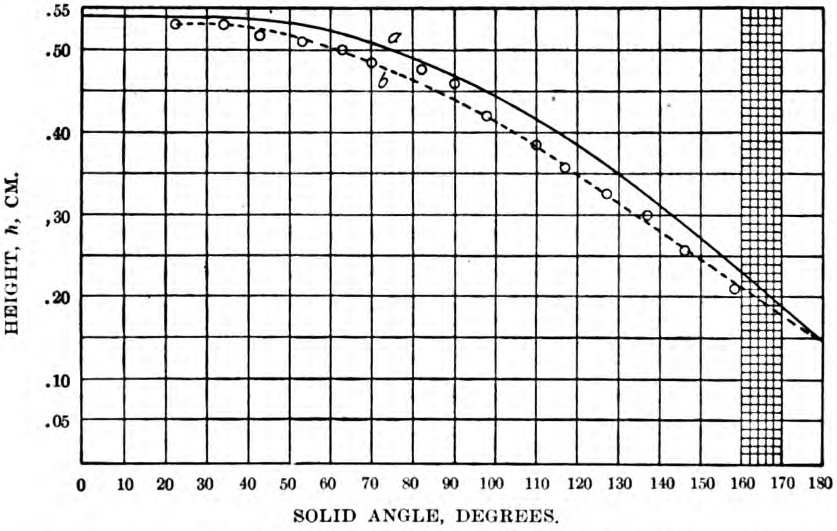

FIGURE 10.—A comparison of theoretical (*a*) and observed (*b*) heights, *h*, at the instant of overflowing, obtained by distilled water on beveled glass plates having stated solid angles.

checks closely the theoretical height. According to the theory evolved during the work, the maximum height of the liquid bore a definite relation to the solid angle. Results in this table are plotted in Figure 10.

TESTS WITH MODIFIED SOLUTIONS ON GLASS PLATES.

In order to study further the effect of banking of liquids at edges, attention was given to solutions or modified liquids.

ETHYL ALCOHOL.

Ethyl alcohol (95 per cent) was investigated as to the heights it will obtain on the glass plates used in the water experiments; it was chosen for at least two reasons. First, the angle of contact of ethyl alcohol against glass is usually given in the literature as 0° or thereabouts. Second, water and ethyl alcohol are mutually soluble in all proportions; the banking effect at an edge might be of the same nature as pure water.

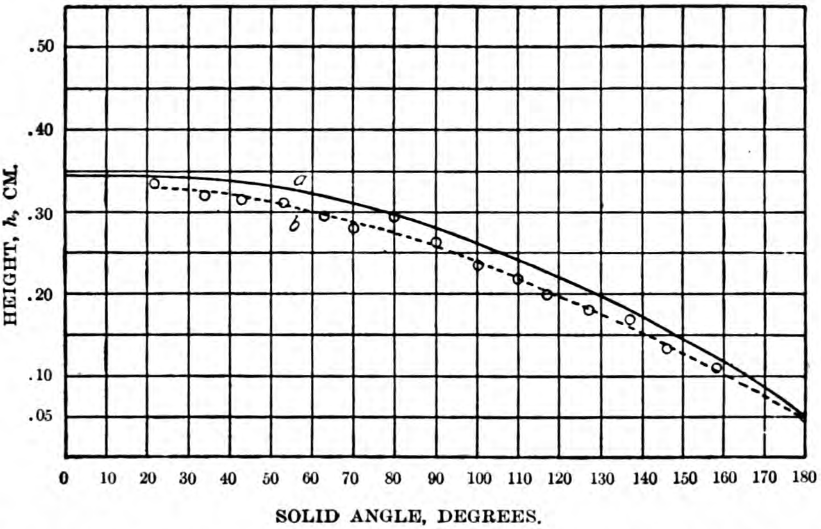

FIGURE 11.—A comparison of theoretical (*a*) and observed (*b*) heights, *h*, at the instant of overflowing, obtained by 95 per cent ethyl alcohol on beveled glass plates having stated solid angles.

The results of the measurements are tabulated in Table 10; and are plotted in Figure 11. The contact angle for the alcohol is 19° as compared with 30° for water. In this table the same points may be noted as in Table 9 for distilled water. The maximum height obtained with the alcohol is much smaller than that obtained for pure water.

TABLE 10.—*Theoretical and experimental values of the heights, h, of ethyl alcohol (95 per cent) on glass plates with stated solid angles.*

(θ=19°; T=0.0295 gm. wt. per cm.; d=0.823.)

Plate No.	Solid angle (degrees).	Height of liquid.		Volume of liquid (c. c.).
		Theoretical (cm.).	Experimental (cm.).	
	180	0.055	0.055	....
	170	.086	....	....
1	159	.117	.110	0.80
2	146	.153	.135	2.00
3	137	.177	.170	3.10
4	127	.202	.180	4.00
5	117	.225	.200	5.00
6	110	.241	.220	5.50
7	98	.265	.235	7.00
8	90	.280	.265	8.00
9	82	.293	.270	8.00
10	70	.310	.285	8.30
11	63	.319	.295	9.00
12	53	.328	.310	9.50
13	43	.336	.315	9.50
14	34	.341	.320	9.30
15	21	.343	.335	9.00
	10	.344	....	....
	0	.344	....	....

CALCIUM CHLORIDE SOLUTION.

Aqueous calcium chloride (10 per cent) solution was chosen as the next liquid for study, because the addition of calcium chloride was known to increase the surface tension of water, and preliminary tests showed that the solution had a larger contact angle (50°) with glass than either water or alcohol. The observations on the calcium chloride solution are recorded in Table 11; the results are plotted in Figure 12.

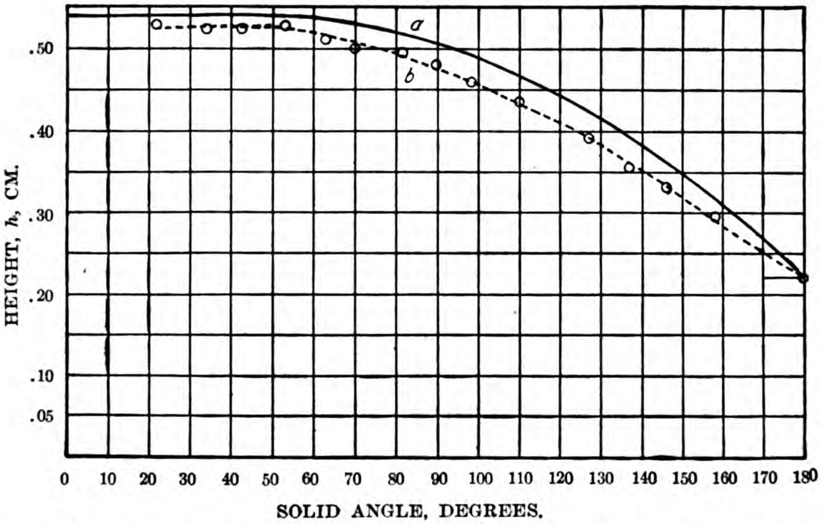

FIGURE 12.—A comparison of theoretical (*a*) and observed (*b*) heights, *h*, at the instant of overflowing, obtained by aqueous calcium chloride on beveled glass plates having stated solid angles.

TABLE 11.—*Theoretical and experimental values of the heights, h, of aqueous calcium chloride solution (10 per cent) on glass plates with stated solid angles.*

(θ=50°; T=0.0788 gram weight per cm; d=1.074.)

Plate No.	Solid angle (degrees).	Height (h) of liquid.		Volume of liquid (c. c.).
		Theoretical (cm.).	Experimental (cm.).	
	180	0.220	0.220	....
	170	.270	....	....
1	159	.314	.295	2.00
2	146	.362	.330	4.50
3	137	.392	.355	6.00
4	127	.423	.390	8.00
5	117	.451	.420	9.50
6	110	.468	.435	10.00
7	98	.494	.460	11.50
8	90	.508	.480	12.60
9	82	.520	.495	13.00
10	70	.532	.500	14.00
11	63	.537	.510	14.60
12	53	.540	.530	14.50
13	43	.541	.525	15.00
14	34	.541	.525	14.60
15	21	.541	.530	13.40
	10	.541	....	....
	0	.541	....	....

SULPHURIC ACID AND PINE OIL SOLUTIONS.

In order to parallel actual flotation conditions more closely in studying the banking of liquids at edges, a sulphuric-acid solution (10 per cent) and a pine-oil solution (a 0.05 per cent oil, about 4 pounds per ton of ore) were made. Cathetometer measurements of the heights of each of these solutions on glass plates are tabulated in Tables 12 and 13 and plotted in Figures 13 and 14. Again, it is noted that the experimental and theoretical heights agree very well, and the heights increase with a decrease in solid angle.

TABLE 12.—*Theoretical and experimental values of the heights, h, of sulphuric acid (10 per cent) on glass plates with stated solid angles.*

(θ=20°; T=0.0735 gram weight per cm.; d=1.064.)

Plate No.	Solid angle (degrees).	Height (*h*) of liquid.		Volume of liquid (c. c.).
		Theoretical (cm.).	Experimental (cm.).	
	180	0.090	0.090	....
	170	.136	....	....
1	159	.178	.165	1.20
2	146	.239	.210	3.00
3	137	.273	.230	4.00
4	127	.311	.270	5.50
5	117	.348	.320	7.00
6	110	.371	.350	8.50
7	98	.407	.395	10.50
8	90	.430	.405	11.10
9	82	.449	.415	11.90
10	70	.476	.430	12.50
11	63	.489	.445	12.00
12	53	.504	.460	12.60
13	43	.515	.460	11.50
14	34	.521	.465	12.00
15	21	.525	.505	12.50
	10	.526	....	....
	0	.526	....	....

TABLE 13.—*Theoretical and experimental values of the heights, h, of pine-oil aqueous solution (0.05 per cent oil) on glass plates with stated solid angles.*

($\theta=25°$; T=0.0601 gram weight per cm.; d=1.0.)

Plate No.	Solid angle (degrees).	Height (h) of liquid.		Volume of liquid (c. c.).
		Theoretical (cm.).	Experimental (cm.).	
	180	0.105	0.105	....
	170	.147	....	....
1	159	.191	.170	1.00
2	146	.241	.225	3.00
3	137	.272	.250	5.00
4	127	.308	.285	6.50
5	117	.340	.340	6.70
6	110	.362	.350	8.40
7	98	.394	.375	11.00
8	90	.411	.400	12.00
9	82	.427	.410	12.00
10	70	.453	.425	12.00
11	63	.463	.445	11.70
12	53	.475	.460	12.70
13	43	.484	.470	13.00
14	34	.487	.470	13.10
15	21	.490	.475	12.80
	10	.490	....	....
	0	.490	....	....

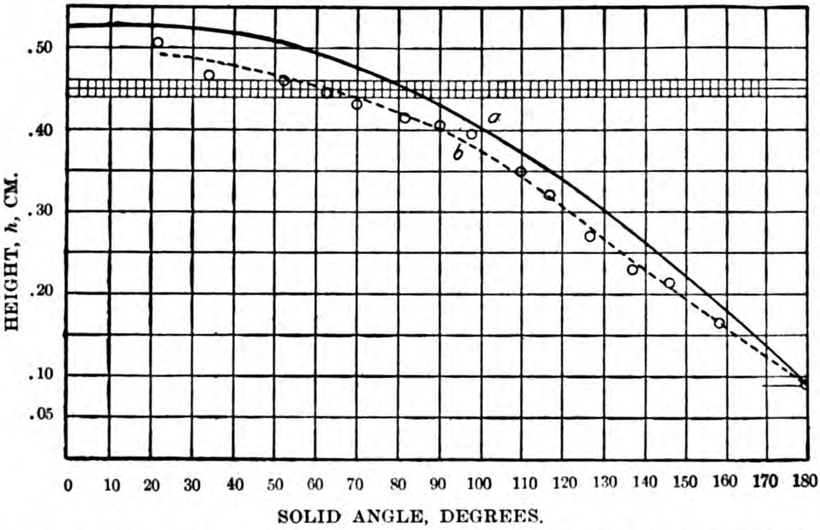

FIGURE 13.—A comparison of theoretical (a) and observed (b) heights, h at the instant of overflowing, obtained by aqueous sulphuric acid on beveled glass plates having stated solid angles.

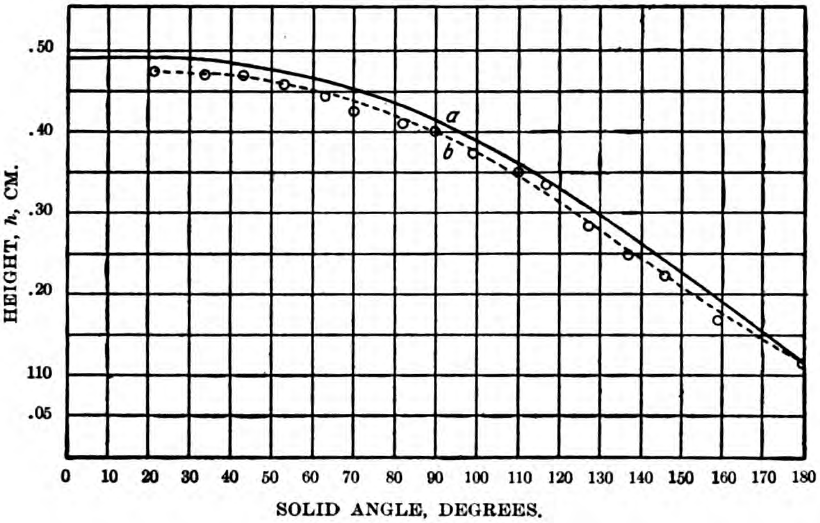

FIGURE 14.—A comparison of theoretical (*a*) and observed (*b*) heights, *h*, at the instant of overflowing, obtained by aqueous pine oil on beveled glass plates having stated solid angles.

SODIUM OLEATE SOLUTION.

With the idea that a solution containing a strongly adsorbed substance might not bank at an edge in accord with theoretical predictions, pure sodium oleate (0.04 per cent) was dissolved in distilled water. The experimental and theoretical heights obtained on the glass plates, as shown in Table 14 and Figure 15, do not agree quite as well as those for the liquids hitherto mentioned.

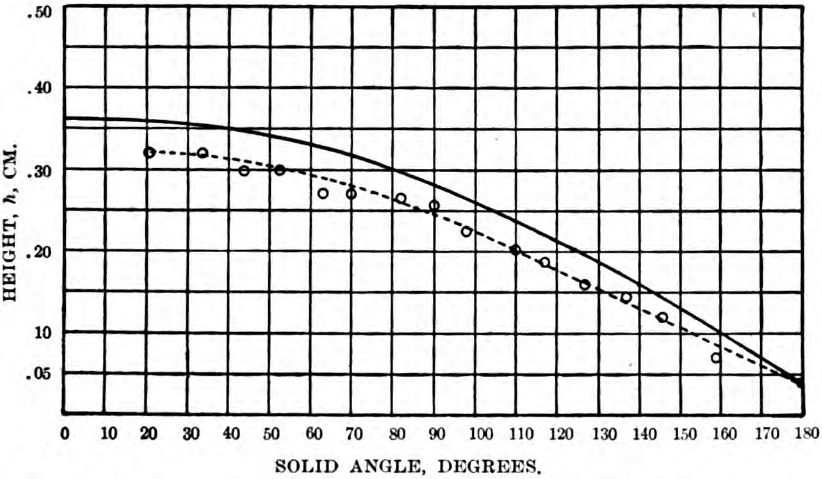

FIGURE 15.—A comparison of theoretical (*a*) and observed (*b*) heights, h, at the instant of overflowing, obtained by aqueous sodium oleate on beveled glass plates having the stated solid angles.

TABLE 14.—*Theoretical and experimental values of the heights, h, of aqueous sodium oleate solution (0.04 per cent soap) on glass plates with stated solid angles.*

(θ=18°; T=0.0327 gram weight per cm.; d=1.0.)

Plate No.	Solid angle (degrees).	Height (*h*) of liquid.		Volume of liquid (c. c.).
		Theoretical (cm.).	Experimental (cm.).	
	180	0.040	0.040	....
	170	.072	....	....
1	159	.105	.070	0.50
2	146	.143	.120	1.70
3	137	.169	.145	2.90
4	127	.191	.160	3.70
5	117	.222	.185	4.00
6	110	.238	.200	5.00
7	98	.267	.225	6.50
8	90	.282	.255	7.90
9	82	.297	.265	7.60
10	70	.317	.270	7.70
11	63	.327	.270	7.90
12	53	.340	.300	8.10
13	43	.349	.300	8.00
14	34	.355	.320	9.00
15	21	.360	.320	8.40
	10	.3616	....	....
	0	.3616	....	....

DISCUSSION OF RESULTS OF "EDGE-EFFECT" EXPERIMENTS.

An explanation of the banking of a liquid at an edge, or the seeming reluctance of the liquid to cross an edge, involves, besides the contact angle, two other things: The equation of the curve representing the profile of a liquid meeting a solid surface, or the profile of a liquid banked upon a plate, and a working definition of an edge.

The equation has been treated in some detail by one of the writers.[6] Either by mechanics or by calculus the contact angle of a liquid against a solid can be obtained by means of the expression.

$$h=2\sqrt{\frac{T}{d}}\sin\tfrac{1}{2}\theta \tag{2}$$

in which h is the height (in centimeters) of the liquid profile, T[7] is the surface tension of the liquid in grams weight per centimeter, d is the density of the liquid, and θ is the contact angle.

DEFINITION OF EDGE.

In the study of flotation principles an edge can not be considered in its strictly mathematical sense as being a line and having only one dimension—length. In the physical sense of the word an edge is here considered as being made up of a number of infinitesimal surfaces of intersection, or as a surface of transition between two planes; it is not simply the line of intersection of two planes. In Figure 16 is an exaggerated sketch of an edge; each dash may be considered as a tiny plane in the edge.

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[6] Anderson, C. O., Thesis, On the physics of ore flotation: University of Washington Library, 1918, pp. 40–56.

[7] A small change in the surface tension of a liquid has only a small effect upon h, as the square root of T enters into the equation. The same holds true for the density.

EXPLANATION OF "BANKING UP" AT AN EDGE—THEORETICAL HEIGHT.

When water is added to the top surface of a horizontal plate, it forms a flattened drop making a definite angle of contact with the solid. As more water is added the drop obtains a definite height before it spreads over the surface; this height substituted in equation (2) gives the contact angle against a horizontal surface. With further additions, the water advances toward the edge, always maintaining this definite height. When the edge is reached, the liquid seems reluctant to cross and begins to bank up and increase its height.[8] What actually happens is this: The liquid, in reality, advances, but with each infinitesimal advance it encounters a change of direction, that is, one of the planes making up the edge. The reluctance is more apparent than real because the water has met a curved convex surface[9] (the edge), which is narrow and changes direction rapidly for each infinitesimal advance across it. The liquid is at all times making an unchanging angle of contact with some one of these planes in the edge; that is, the liquid makes an angle of contact, say 30°, with a plane which is tangent to this curved surface along the mathematical line that represents the intersection of the solid, liquid, and air. In Figure 17, *d* represents a point in the line of intersection of the three substances, solid, liquid, and air; *cd* represents the extension of a plane containing the line of intersection (*cd* is tangent to the solid); *ad* is a plane drawn tangent to the water profile at the

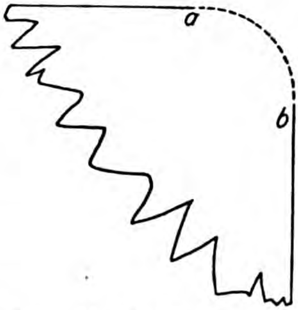

FIGURE 16.—Sketch of an edge of a plate. The dashes may be taken to represent the traces of the hypothetical planes making up the edge.

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[8] Hardy in "The spreading of fluids on glass": Phil. Mag., ser. 6, vol. 38, July, 1919, p. 52, mentions but offers no explanation of the effect of an edge on a drop of acetic acid when he says: "When more than one drop of acetic acid is present on a plate at 18° C., the existence of an invisible film about them is manifested in a curious way. Drops which are not more than one or two centimeters apart attract one another. They become oval in outline, the long axes being directed toward one another, and slowly move across the plate until they meet and fuse. *The edge of the plate acts like another drop*, a single drop tends to move to the edge and cling there, but the edge does not attract it so strongly as does another drop." Is it not possible that Hardy encountered the same effects of an edge as are considered in this discussion?

[9] Two types of edges must be recognized, namely, convex, as at the top of a tumbler, and concave, as at the inside bottom of a tumbler. Reluctance appears with the former and acceleration with the latter.

line of intersection, and *cda* is the contact angle, whose value is probably the same as when the liquid advanced at a constant height across the surface of the plate. The height, *h*, of the liquid is now equal to that height of profile which corresponds to an angle of contact, *cda*+*cfg*, with a horiozntal surface; or, stated conversely, the liquid profile has developed to that height which it would if it were making a contact angle, *eda*, with the horizontal. To be sure, the limit of development of liquid profile has a definite maximum value; this value is attained when the angle of contact becomes equivalent to 180° against a horizontal surface.

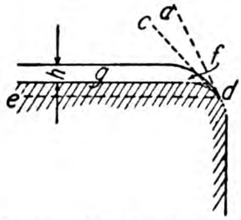

FIGURE 17.—Sketch indicating the conduct of water as it crosses an edge. The edge is exaggerated for illustration and is represented by dotted curved lines.

When a liquid has crossed an edge, it meets the other plane surface (the side of the plate) and flows down the side, because there is no longer a change of direction of solid surface to permit further development of its profile with increasing head of liquid. Thus it is seen that the maximum height at which a liquid (with a given contact angle) will stand on a plate depends on the "dip" of the face that the liquid meets after crossing the edge.

How the theoretical heights of liquid on a plate are obtained is best shown by a few comments on Table 15, which gives the heights water will attain on a horizontal surface with angles of contact ranging from 0° to 180°. The formula $h=2\sqrt{\frac{T}{d}}\sin\frac{1}{2}\theta$ was used to calculate these heights. If the angle of contact is zero, h is zero; the liquid spreads over the solid surface in a thin film. The heights, h, increase as a sine function with an increase in θ. When θ is 180°, the maximum water height (0.54 cm.) physically possible is obtained.

TABLE 15.—*Values of heights of water, h, on a horizontal surface corresponding to values of the contact angle.*

(Calculated from $h=2\sqrt{\frac{T}{d}}\sin\frac{1}{2}\theta$; T=0.073 gram weight. per cm.; d=1.)

Contact angle, θ (degrees).	Liquid height, h (cm.).	Contact angle, θ (degrees).	Liquid height, h (cm.).
0	0	100	0.413
10	.047	110	.442
20	.094	120	.467
30	.139	130	.489
40	.184	140	.507
50	.228	150	.521
60	.270	160	.532
70	.309	170	.538
80	.347	180	.540
90	.382		

Let a contact angle of 30° be assumed. Then the water will stand at a height of 0.139 cm. on a horizontal surface before advancing. If the water meets an edge having a solid angle of, say 140° (See Fig. 18), then the height obtained before the water runs down the side will correspond to the angle (180°—140°)+30°; that is, to the supplement of the solid angle plus the angle of contact against the horizontal surface. This is equivalent to a height (0.309 cm.) corresponding to a contact angle of 70° with the horizontal. Thus for this particular plate with a solid angle of 140°, the maximum theoretical height of water obtainable on its surface is found by substituting 70° for θ in $h=2\sqrt{\frac{T}{d}}\sin\frac{1}{2}\theta$ and solving for h. This method was employed in calculating the theoretical h in Tables 9 to 14, inclusive.

One point should be noted in regard to the solid angle, Figure 18. The statement has been made that the heights of liquid obtainable depend on the dip of the side. When the supplement of the solid angle plus the contact angle (30°) equals 180°, then h will have its maximum physical value; it is not possible for the profile to reach a greater height. When these two angles exceed 180°, h will have the same value as when they equal 180°. Thus two plates with solid angles of 30° and 20° (contact angle 30°), will have the same h—namely, 0.54 cm. Consequently, there is a certain range within which the heights do not strictly depend on the solid angle of the plate; when the dip of the plate gives a solid angle less than the contact angle, h will have a constant value—that is, its maximum value. This is brought out graphically by the straight horizontal portions of the curves marked "theoretical" in Figures 10 to 15, inclusive.

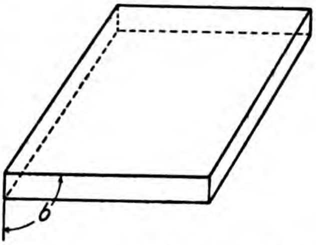

FIGURE 18.—Sketch showing the angle *b*, the so-called solid angle.

The reader is now in a position to review the data recorded in Tables 9 to 14, and Figures 10 to 15, with more facts at his command.

Various methods of measuring the angle of contact were discarded in favor of the one used herein—namely, the measuring of h when the height is constant as the liquid advances across a horizontal surface and before it reaches an edge. Thus in Table 9 the first figure under "experimental h" (column 4) is 0.14 cm., which is the height of water on a horizontal glass plate when the solid angle is 180°. Of course, this same value, 0.14 cm., appears under "theoretical h," as it determines the angle of contact of water against glass; for this reason the theoretical and experimental curves in Figures 10 to 15 have one point in common—that is, when the solid angle is 180°. So in Tables 9 to 14, the first number under experimental h is the height

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measured when the liquid is advancing across a horizontal surface, and represents the angle of contact of that particular liquid with glass, as recorded in the headings of these tables.

The experimental results are always less than but check closely the theoretical heights. Difficulties in carrying out the experiments readily explain how these heights do not reach their theoretical values. It was difficult to get the plates in an absolutely horizontal position. The liquid was carefully delivered to the plate surface, but the slightest force from the oncoming liquid was sufficient to push the liquid over the side of the plate before attaining the height theoretically possible. Also, the heights were measured from the top surface of the plate upward, whereas the bottom edge of the liquid was slightly lower, for it had begun to cross the edge of the plate.

The maximum theoretical height for water is 0.54 cm., whereas the greatest height reached in tests was 0.53 cm. This is within 2 per cent of the theoretical. Such close agreement between the experimental and theoretical heights in columns 3 and 4 of the tables justifies the explanation offered, at least for a pure liquid, like water, on glass.

Plate I, *A*, shows water resting on a beveled plate of glass. The depth of water is 0.46 cm. The water is at the point of breaking over the edge. The profile of the liquid has reached a height not far from the physical maximum.

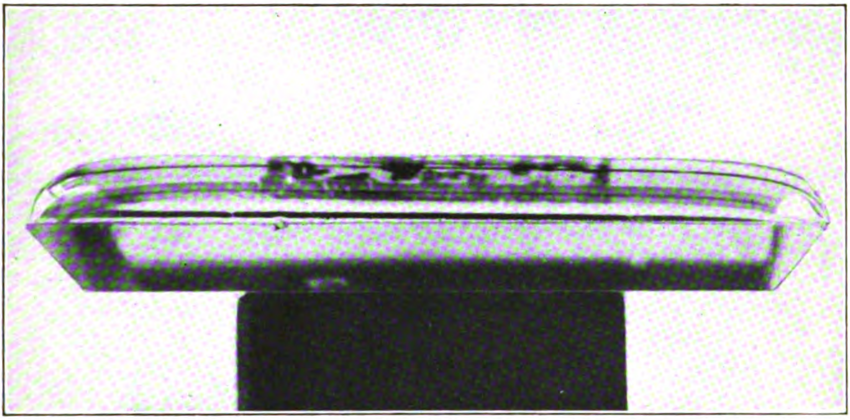
In Figure 10, plotted from the results in Table 9, the curves lie very close to each other, thus showing a close agreement of experimental with theoretical values. They have the general shape of sine function curves with the exception of the horizontal straight portion (p. 32).

In the five modified liquids investigated, ethyl alcohol, aqueous calcium chloride, sulphuric acid, pine oil, and aqueous sodium oleate, the heights check each other much the same as they did for distilled water.

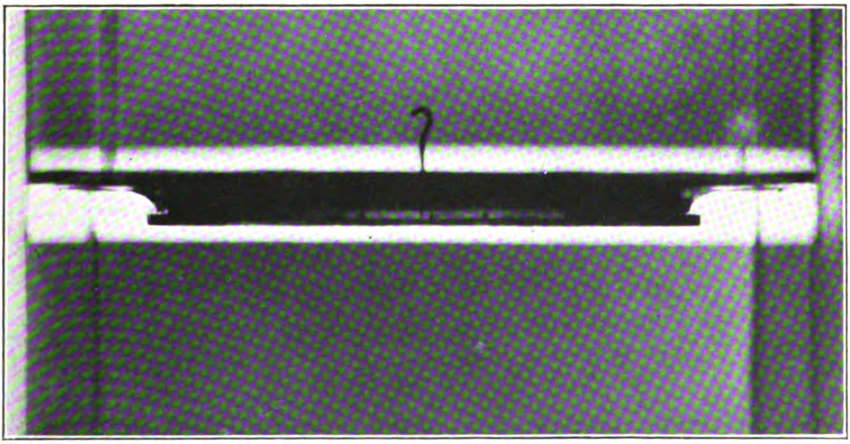
Ethyl alcohol (Table 10) has a smaller contact angle with glass than water, 19° as compared to 30°; the maximum height for alcohol is 0.344 cm. as compared to 0.54 cm. for water. This latter result is accounted for by the fact that the surface tension of alcohol is much less than that of water.

Aqueous calcium chloride (Table 11) has a larger contact angle (50°) than water; the sulphuric acid solution (Table 12) has a smaller one. The former solution has a maximum height of 0.541 cm. and the latter 0.526 cm.

The observations on a 0.05 per cent aqueous pine-oil solution (Table 13) are interesting, as this strength of solution is roughly approximate to the strength often used in the flotation of ores. The angle of contact is 25° as against 30° for water. The maximum height is 0.49 cm.



A. WATER ON THE SURFACE OF A BEVELED GLASS PLATE.



B. GROOVED GLASS PLATE LOADED WITH SAND AND RAFTED ON WATER BY "FILM-SUSPENSION."

For some reason, possibly an adsorption effect, the heights for a soap solution (Table 14) did not check the theoretical values as closely as in the preceding tests. The results, however, are believed to accord with the explanation given of the edge effect in the banking of water on a plate.

Any application of this work directly to flotation must be to bodies floating on a plane and tranquil surface. The logical procedure is to study the floating of bodies on plane and tranquil surfaces before taking up the study of floatability of bodies which are on curved and disturbed surfaces, as in the flotation cell.

EXPLANATION OF THE OVERFILLED TUMBLER.

A logical explanation of the conduct of water in overfilling a tumbler is now readily made.[10] When the vessel is partly full, the surface of the water makes its contact angle of, say 30°, with the glass wall. When the vessel is "level full," the contact angle is still the same; the water surface makes the angle of 30° with some plane in the edge, as before explained. As the vessel is overfilled the same angle is being made with some plane in the edge. The water will advance over the horizontal space between the inner and outer edges of the tumbler when that height (0.139 cm.) has been attained which is equivalent to an angle of contact of 30°. When the water reaches the outer edge, it banks up until the height, 0.467 cm., is obtained (equivalent to an angle of contact of $30°+90°$ with a horizontal surface), when it will flow down the vertical side.

EXPLANATION OF THE FLOATABILITY OF GLASS PLATES.

The preceding explanation accounts for large plates of window glass being so easily floated. The water will not advance across a surface (plane or curved) until the liquid profile has been so developed as to make an angle of say, 30°, with that surface. This statement suggests the possibility that if a plate possessed an edge so designed that the liquid profile would be developed to a maximum, the plate would be more floatable; the greater the liquid height, the greater is the hydrostatic head that acts upward to aid in floating the plate. This inference was found to be true.

DESIGN OF AN EDGE FOR MAXIMUM FLOATABILITY.

To design the proper edge for a plate for maximum floatability becomes easy when one remembers that, in the measurement of liquid heights on glass plates, the maximum physical height was developed when the dip of the side made a solid angle equal to or less than the contact angle of the liquid. Accordingly, a groove around a circular plate (Fig. 19) was so made that the reentrant angle D was equal to or less than the contact angle; a floating plate 7.7 cm. in diameter and 0.14 cm. thick can be loaded with 10 grams of sand before sinking.

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[10] The writers briefly discussed the overfilled tumbler and the reluctance of a convex edge to allow a liquid to cross it in the Scientific American Supplement, July 27, 1918, p. 52.

A photograph (approximate actual size) of a loaded glass plate rafted on water in a square glass box is shown in Plate I, *B*. The hook that shows above the surface of the water was glued to the center of the plate and used to launch it. The photograph shows strikingly the height of the liquid profile meeting the plate. The water has crossed the outer edge of the plate and is hinged on the edge of the groove.

When the reentrant angle (solid angle) is equal to or less than the contact angle, the maximum depth of the dimple for a floating plate is 0.54 cm., and the hydrostatic head acting upward on the plate will obviously be 0.54 grams per square centimeter of plate surface. Theoretically, if the glass had a surface of infinite area, it would float a load of infinite weight. There are, however, two limiting factors: Large liquid surfaces are not tranquil enough; and grooves that will fulfill specifications are difficult to grind. As regards the latter difficulty, a circular plate is the easiest to prepare because sharp turns can be avoided. However, a glass plate 3½ inches broad and 8 inches long has been floated readily. The ends are pointed like those of a boat, and are paraffined because the grooves can not be cut there.

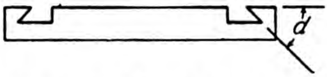

FIGURE 19.—Vertical section of a glass plate grooved for maximum floatability.

DIFFERENCE BETWEEN FLOATABILITY OF CYLINDRICAL AND PRISMATIC BODIES.

Again may be emphasized the difference between the floatability of cylindrical bodies and those having plane faces. Furthermore, a plate with an edge designed properly is as floatable when the angle at which the liquid meets the solid is so small as 1 degree as it is when the angle is much larger.

The reason for this statement will be more evident after consideration of the curves in Figure 20. These curves represent the theoretical heights, h, of distilled water for various contact angles on horizontal surfaces with various solid angles; they were plotted by means of Table 15 and the formula, $h=2\sqrt{\frac{T}{d}}\sin \frac{1}{2}\theta$. They correspond to the theoretical curves plotted for the various liquids in Figures 10 to 15. The lowest curve gives the theoretical heights of water for a series of plates when the angle of contact of water with the solid is 1°; the next curve is for a contact of angle of 10°, and so on. Table 15 may be used for the determination of the values

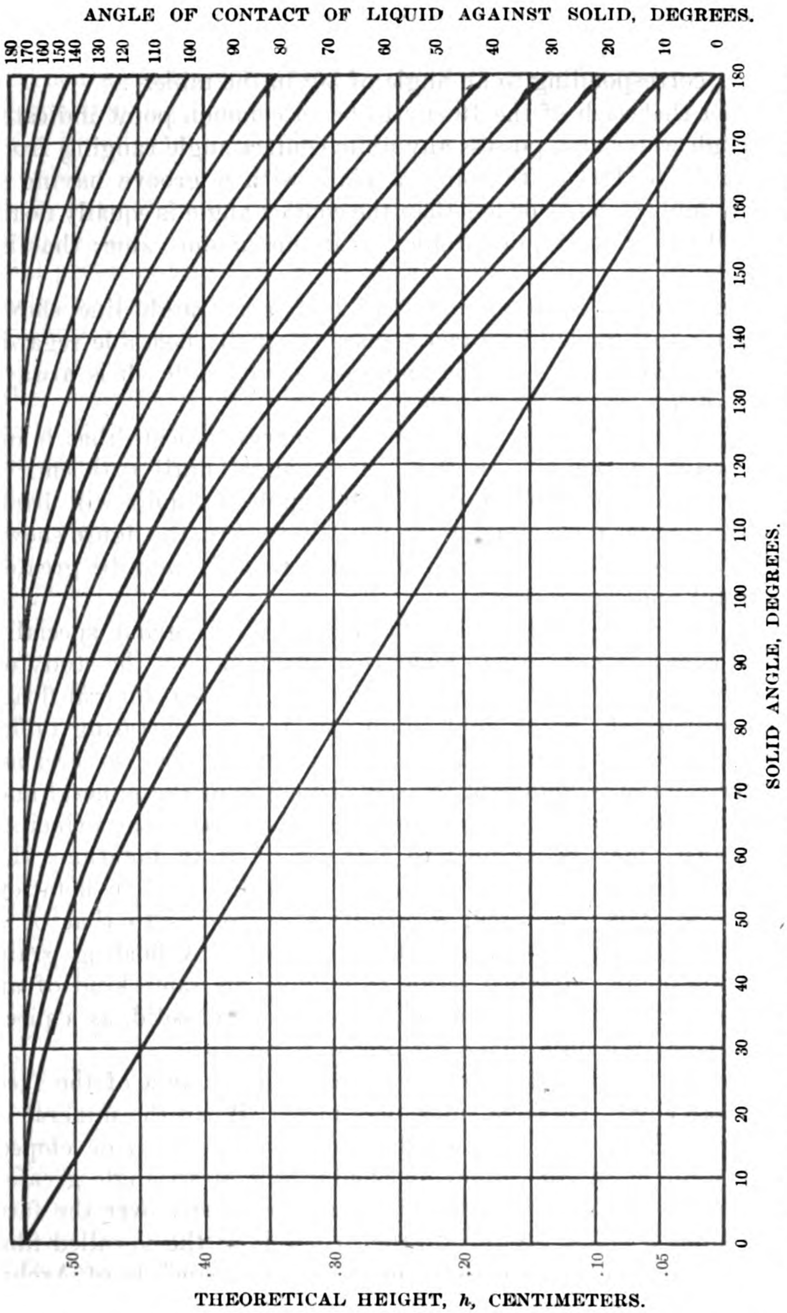

FIG. 20.—Theoretical heights, *h* (ordinates) of distilled water with stated contact angles on horizontal surfaces with beveled edges having stated solid angles (absissae).

represented by each curve. Thus, for the point on the second curve (contact angle, 10°) representing a solid angle of 170°, the value (180−170)+10 is substituted for θ in the above formula, and gives 0.094 cm., as shown in the table (column 2), opposite angle of 20°.

Again, for the third curve, angle of contact 20°, and solid angle 170°, substituting the value of (180−170)+20 for θ in the formula gives 0.139 cm., corresponding to an angle of 30° in the table.

The fact that each of the 19 curves has a common point indicates that though water may possess any finite contact angle ranging from less than 1° to 180° with solids a plate with a groove having a reentrant angle equal to or less than the contact angle is equally floatable in all cases; the liquid profile has its maximum value; that is, 0.54 cm.

The curve for an angle of contact of 180° is a straight line, showing that for this angle of contact a plate is equally floatable regardless of its solid angles. If the angle of contact is 0°, h is always zero, regardless of the solid angle.

For a given solid angle, say 110°, the curves indicate that h increases with an increase in the contact angle until 0.54 cm. is reached; on a plate with a given solid angle a liquid will bank higher the greater the contact angle is. Conversely, the figure shows that for a given h, say 0.30 cm., the contact angle must be greater as the solid angle increases.

Though one can hardly advise metallurgists to grind specially designed edges on minerals to make them floatable, yet the study of the principle of edge effect is advantageous. When a mineral floats by film suspension in the gold sluices, on the concentrating table, and on the film-suspension flotation machine, it does so because the water solution is reluctant to cross the edges of the mineral and advance over the upper face. It seems consistent that the principle of edge effect may be applied to a study of froth flotation; the bubble attached to a mineral grain, so much discussed in flotation literature, appears to present a condition analogous to that of a mineral floating on the plane surface of water. A floating grain with an air bubble attached seems to involve the same kind of an equilibrium of the three substances, water, air, and solid, as a piece of mineral floating on a plane surface of water.

The weight of solid floatable increases with the area of the face along whose edges the three substances meet. When the mineral is too heavy to float, the profile of the water surface is so developed that the water meets the upper horizontal face at an angle greater than the contact angle; consequently, the water passes over the face and the mineral sinks. After all, the principle of the so-called film suspension of minerals is closely related to the principle of Archimedes (any body immersed in a liquid must lose weight equal to the weight of the displaced liquid), because it depends partly on the amount of water displaced; an edge makes a barrier along which the liquid forms a wall until the liquid obtains sufficient height to flow over the top of the mineral. *The effect of this barrier vanishes*

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only when the contact angle is zero, and only then is the mineral absolutely nonfloatable.

The maximum height that this wall of liquid may obtain is directly proportional to the square root of the surface tension of the liquid; if a liquid had practically zero tension no appreciable liquid wall would be possible at an edge. Surface tension is responsible for this wall, but exerts little effect in balancing the weight of a fairly large floating body. Though these observations do not solve the commercial problem, they add to the knowledge of floating bodies and should help the development of a science of flotation.

Before the advent of flotation the metallurgist's difficulties included the prevention of the floating of flaky minerals. Though this property of flaky minerals has been commonly known for a long time, its explanation has been wanting. It is now obvious. It is based on the aforesaid edge effect; the conclusion is that for a given mass the floatability of mineral (and of a glass plate) increases with the area of the face along whose edge the three substances (liquid, solid, and air) meet. The buoyant effect of a given head of water depends entirely upon the area of the face exposed to the air and is, therefore, independent of the shape of the face. With large faces the upward pull of the surface-tension film may be neglected, but with small faces it is a factor; the conclusion follows that with small faces of various shapes, the solid with an oblong face—that is, the greatest length of edge—exposed to the air is most floatable.

RELATION OF THE CONTACT ANGLE TO THE CONFIGURATION OF THE SOLID SURFACE.

Before this discussion of the observations of the contact angle is closed, a phenomenon not easily classified, but which may be of great importance in flotation, will be recorded.

A plate was prepared by dipping it in molten paraffin; then powdered galena (through 150 mesh) was sprinkled over its surface. This prepared plate was pushed vertically into water. The angle of immersion was 160° (the angle of emersion was 130°). This result was surprising because tests with a piece of galena having a large plane surface exposed showed a much smaller angle of immersion, 45° to 60°. The paraffin did not vitiate the results by filming the mineral particles as the contact angle of water against paraffin is about 90°, and the galena was sprinkled on the plate quite thickly. The powdered galena and the massive galena each has its hysteresis of contact angle, but this is of minor importance compared to the striking difference of their respective angles of immersion or of emersion as a result of a change in the state of aggregation. Apparently this striking difference is an exhibition of the aforementioned edge effect; the contact angle in this case is the mean result of the effect of all the convex edges of the tiny sulphide particles.

This may be a factor in the flotation of granules or floccules; when a number of particles are close together their many edges may cause the solution to seem to make a large contact angle. It was obvious that the liquid did not penetrate the concavities among the powdered galena grains, but entrapped air by passing to successive projecting edges, as was revealed by the silvered appearance of the submerged plate. The entrapped air forms nuclei for bubble formation which, if this state of flocculation exists in the cell, is an important consideration in flotation.

SPREADING OF LIQUIDS ON SOLIDS.

The contact angle is closely related to the subject of spreading of a liquid on a solid surface. Reference is again made to formula (1) discussed in the early part cf the paper. If the tension $T_{w,a}$ equals or exceeds $T_{w,o}+T_{o,a}$, the angle θ becomes zero, and what is known as "spreading" or "wetting" occurs. Obviously the essential conditions for the wetting of a solid by a liquid are that $T_{w,a}$ shall exceed $T_{o,a}$ and that $T_{w,o}$ shall be less than their difference; that is, the tension at the interface shall be less than the difference between the surface tensions.

SPREADING AS APPLIED TO AMALGAMATING, TINNING, GALVANIZING, OR LEADING.

The knowledge of the inequality mentioned above may be applied in making pertinent conclusions, such as the following: In amalgamating, tinning, galvanizing, and leading the energy of the solid surface, $T_{w,a}$, is undoubtedly greater than that of the spreading liquid; the well-known wetting power is evidence that the interfacial energy is less than the difference of the surface energies of the liquid and of the solid. Table 16 shows these combinations. The surface energies of the "solids" at working temperatures are considerably greater than those shown in the table, because the surface tensions given are for temperatures just above the melting points of the metals; the surface energies in the solid state are surely much greater than in the liquid state. Copper at 1,100° C. has a tension of 580 dynes per centimeter; at 15° C., when mercury ($T=436$) spreads on it, the copper has a greater surface tension than the mercury. The table shows that the solids, even at the high temperatures indicated, have a higher tension than the respective spreading liquids. On the assumption that the interfacial tension of any pair of these substances is quite small, 100 dynes or less, the so-called spreading liquid would spread on the molten metal even at the high temperatures, unless the temperature is above the boiling point of the liquid.

TABLE 16—*Minimum values of the surface tension (energy) of solid metals which are wetted by the respective metals in the liquid state.*

No.	Solid.			Spreading liquid.		
	Metal.	Temperature (°C.).	Surface tension (dynes per cm.)	Metal.	Temperature (°C.).	Surface tension (dynes per cm.)
1	Copper	1,100	580	Mercury	15	436
2	do	1,100	580	Tin	250	352
3	Gold	1,070	612	Mercury	15	436
4	Iron	1,200	1,000	Zinc	360	877
5	do	1,200	1,000	Tin	250	352
6	do	1,200	1,000	Lead	330	448

To state that if nature had reversed the order of the melting points of the "solid" and the "spreading liquid" amalgamating, galvanizing, tinning, or leading would be impossible is merely stating a truism. On the other hand, the use of this table to predict that if nature had similarly reversed the surface tensions these processes would likewise be impossible is to employ well-founded theories of surface tension (surface energy).

As it is with water, so it is with solid metals, perfectly clean surfaces with maximum surface energies are difficult to obtain because of the abundance of contaminating fluids giving interfacial tensions which are greater than the difference between the surface tensions, the condition of nonspreading. The quantity of the contaminant may be minute but yet enough to alter $T_{w,a}$ so that it is not greater than $T_{o,a}+T_{w,o}$; then the "spreading substance" becomes an inhibitory film.

As is well known, a copper plate must be thoroughly cleaned before mercury will spread on it. When a fresh surface is once obtained—a surface of high surface energy—the mercury spreads freely and adheres with such tenacity that it defies even fire. The amalgamator says that it "bites." Liquid zinc will not bite an iron wire unless the surface of the wire is freed of all impurities. When the wire is clean, the zinc spreads freely and a galvanized surface is the result. Mercury spreads freely on gold when there is no contaminating film.

IS SPREADING A CHEMICAL OR A PHYSICAL ACTION?

Some may regard amalgamating, galvanizing, etc., as chemical rather than physical, and therefore object to this classification. The barrier, however, is more seeming than real. Langmuir,[11] in speaking of the distinction between chemical and physical phenomena, says:

> In gases there is usually no uncertainty as to the size of the molecules, but in liquids and solids no really satisfactory methods have been found for determining molecular weights. So long as we can not definitely determine the

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[11] Langmuir, Irving, Constitution and fundamental properties of solids and liquids: Jour. Amer. Chem. Soc., vol. 38, 1916, p. 2225.

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molecular weights, it thus remains impossible to distinguish sharply between chemical and physical phenomena. Nevertheless, much discussion has arisen of late years over such questions whether adsorption and surface tension are chemical or physical phenomena. The overwhelming consensus of opinion seems to be that these are both physical phenomena. In the following pages the writer hopes to show that there is no present justification for this distinction between chemical and physical forces. Cohesion, adsorption, and surface tension are all manifestations of forces similar in their nature to those acting between the atoms of solid bodies. It is, therefore, advantageous to look upon these forces as direct results of chemical affinity.

Seemingly, there are no sharp lines of demarcation between chemical and physical forces, and our knowledge of them may be applied separately or collectively as the case demands.

Any one who wishes to regard spreading as a chemical phenomenon caused by dissolution at the interface will find justification for that conception in Table 6 (p. 16), where comparison is made of the mutual solubilities and interfacial tensions of the two groups of liquids enumerated. There it is obvious from a knowledge of solubilities that low interfacial tension accompanies solubility and that high interfacial tension accompanies insolubility. If one's adherence to the idea that the forces controlling spreading are chemical proves to be a guide in an investigation, well and good; but if he discards the data on surface and interfacial tension he cuts the communication between himself and a group of scientific workers who measure the thing about which they are talking and give it a numerical value, without which, according to Lord Kelvin, the knowledge is meager and unsatisfactory.

The mutual solubilities of the pairs copper-mercury, copper-tin, gold-mercury, iron-zinc, iron-tin, and iron-lead, which are shown in Table 16, are known. As it is with a pair of liquids, so it is with a pair of substances of which one is a solid; solubility causes a blending at the interface which reduces the tension, until, when there is complete solubility, the interface vanishes, and with it vanishes interfacial tension. The more interfacial tension is reduced by chemical change the more likely is $T_{w,a}$ to be greater than $T_{o,a}+T_{w,o}$, which signifies spreading.

Another fact bearing on the chemist's versus the physicist's view of spreading is that platinum does not amalgamate with pure mercury.[12] The chemist would probably dismiss this consideration with the statement that it is due to insolubility. The physicist notes that platinum has a surface tension of 1,658 dynes per centimeter at 2,000° C., or enough for mercury to spread on it, but as the phases are insoluble it is probable that $T_{w,a}<T_{w,o}+T_{o,a}$, and under these circumstances

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[12] The three phases, solid platinum, liquid mercury, and gaseous air, are considered here. To be sure, platinum may be coated with mercury by electrolytic deposition from the pure nitrate or other solution of mercury, but in that event the three abovementioned phases are not coexistent.

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it is impossible for mercury to spread. A regard for both physical and chemical properties would seem to be of more service in predicting results than a method in which only one set of these properties is considered.

SPREADING AS APPLIED TO COAL-DUST SPRAYS.

As has been said above, spreading may be facilitated by the removal of the inhibitory film. Sometimes removal of this film is not feasible, but recourse may be had to an alternative. In this alternative, the liquid may be modified by a substance which will alter $T_{o,a}$ and $T_{w,o}$, and spreading may thus be accomplished.

The force, $T_{w,a}$, at the surface of coal is not enough to make pure water spread freely upon coal. This spreading is desirable in sprinkling coal mines, but it is not feasible to increase $T_{w,a}$ by polishing the coal surface, as is the custom with a copper plate, or by using acid, as in galvanizing; so $T_{o,a}$ and $T_{w,o}$ must be changed. This change is accomplished by adding soap to the water, when spreading results.

The coal miner has applied these principles to commercial work and gives the following explanation:[13]

> These dust-laying processes have been duly considered by Dr. Thornton, who has made experiments favoring the view that an efficacious spraying mixture can be made with soap and water. He demonstrated that the whole question of the wetting of dust was one of surface tension of the liquid used, and that the water alone did not possess the property of readily wetting the coal dust, unless indeed it was used in large quantities. On the other hand, the soap and water mixture completely wetted the dust, turning it into a liquefied form of mud, the chief component of which was coal dust.

SPREADING OF DETERGENTS.

The incorporation of these principles into the science of detergents, according to Hillyer,[14] antedates its application in coal mining. What he suggested in 1903 as a "possible factor" in the principles of detergents is now a generally accepted fact.

> We have seen before that another possible factor in cleaning, namely, the power which soap solutions have of wetting oily substances, is due to the soap itself. But this wetting power may be experienced only by the strong adhesion of the soap to the oil and the cohesion of the soap solution itself. The latter will more easily spread out over the surface if its cohesion is small, and a stronger force will be acting to spread it out if it is strongly attracted to the oily surface.

In flotation much has been written about oil spreading on water, but, as noted by Hillyer, the soap specialist must make a water solution that will spread on oil, otherwise his soap is a failure. Indeed, the soap acts as a solvent on certain oils, but in addition to its solvent effect the spreading and lubricating power of the soap solution is essential. Soluble dirt is only one form of dirt. There are many others, and they must be lubricated by a spreading or wetting liquid before they will slip off the fiber. If they slip off and become permanently suspended in the soap solution, the cleansing of the fiber is complete.

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[13] Eng. and Min. Jour., Sprinkling of coal mines, vol. 94, 1911, p. 531.

[14] Hillyer, W. E., On the cleaning power of soap: Jour. Am. Chem. Soc., vol. 25, 1903.

SPREADING OF ANIMAL DIPS AND HORTICULTURAL SPRAYS.

Knowledge of the principles governing the spreading of liquids is fundamental in flotation. In the tardy recognition of their importance mining engineers do not stand alone. Agricultural chemists have been equally tardy.

Cooper and Nuttall[15] write very interestingly about this while discussing the subject of dipping and spraying solutions.

> No proprietary dip is now recognized unless the manufacturer can furnish a field tester, by means of which the stock breeder can himself determine in a simple and fairly trustworthy manner the percentage of active constituent in his bath. The underlying idea upon which all these regulations are based is that the principal factor, which determines the efficacy of a dipping fluid, is the quantity of toxic substance present. It has been shown, however, in experience derived from field experiments and routine dipping that this assumption is unwarranted. There is another factor of almost equal importance, namely, the capacity of the dipping fluid to wet the greasy hide or fleece. The fact that the Queensland official dip contains soap as a basis may be quoted as an indication that the importance of the wetting power of dipping fluids is recognized in actual practice.

Continuing, they say:

> What has been said of dipping fluids refers with equal force to horticultural spraying fluids—a high percentage of toxic substance is no criterion of the efficiency. The supreme importance of the spraying fluid having a high wetting power is gradually becoming more and more recognized, though not generally by Government authorities. In the United States compulsory spraying is rapidly becoming the rule, and the standardization of spraying fluids as its natural consequence. This standardization merely considers the percentage of toxic agent and entirely disregards the equally important point of the wetting power.

Though castor oil spreads on pure water ($\theta=0$), Cooper and Nuttall give the results of tests wherein they modified the water and made it spread on castor oil. To do this they placed a strong soap solution on a plate which had been smeared with castor oil. A comparison of the surface tensions shows that spreading of the soap solution is favored, but, as has been stated, spreading does not necessarily follow unless the interfacial tension is less than the difference between the surface tensions. These writers further say:

> Solutions containing respectively 10.0, 1.0, and 0.1 per cent of oleic-acid soap all possess practically the same liquid-air surface tension. (This is known

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[15] Cooper, F. W., and Nuttall, W. H., The determination of the wetting power of dipping and spraying fluids: Jour. Agric. Sci., vol. 7, 1915, p. 219.

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to be about 24.5 dynes per centimeter.) If their wetting powers be tested by their capacities to form a continuous film on a piece of greased paper, it will be found that the 10.0 and 1.0 per cent solutions give positive results, whilst the 0.1 per cent solution entirely fails to wet.

Contamination will unfailingly produce a spreading liquid if the surface tension is not too high and if the interfacial tension approaches zero as the proportion of contaminant present increases.

SUMMARY AND CONCLUSIONS.

1. The Neumann equilibrium triangle can not be used in a consideration of the interfacial forces of a system containing a solid, a liquid, and a gas, but by coordinating the surface energy of a solid with the surface tension of a liquid, an equation containing the angle of contact of a liquid with a solid may be used. The angle of contact bears the same relation to the interfacial energies of the system, solid—liquid—gas, as the Neumann equilibrium triangle does to the interfacial tensions (or energies) of the system, liquid—liquid—gas.

2. A review of the writers' previous work on the relation of the angle of contact to the floatability of cylindrical objects has been given. The angle of contact may have any value, however small (except it be not zero), and a substance will be floatable providing its radius is small enough. The value of the surface-tension force is only a part of the total upward forces acting when a cylinder is floating.

3. The phenomenon of the overfilled tumbler has been described; the water has many menisci, some concave and some convex, and, therefore, apparently has an infinite number of angles of contact with glass, giving rise to an anomalous condition. This is explained as being the result of the effect of the convex edges, whereby they are reluctant to allow a liquid to cross them. The contact angle in reality remains constant while water fills and overfills the tumbler.

4. Study of a small overfilled tumber set within a larger one into which water was poured until its meniscus turned down to the outer edge of the smaller tumbler, formed the basis for the prediction that glass prisms were floatable; even large plate-shaped prisms were found to be floatable.

5. The difference in size of floatable bodies of cylindrical shape and of prismatic shape is distinctly brought out by the fact that the largest aluminum cylinder (specific gravity 2.7) floatable under the best conditions has a radius of 0.23 cm., whereas a clean glass plate (specific gravity 2.6) 0.3 cm. thick is floatable under certain conditions even if the plate had infinite breadth and length.

6. The edge effect was studied by making cathetometer measurements of the heights attained, before overflowing, by pure and modified liquids on beveled glass plates having various solid angles.

7. From a consideration of the curve representing the profile of the surface of a liquid meeting a solid and of the angle of contact the theoretical heights that liquids will attain on horizontal plates before overflowing were determined. Experimental measurements checked the theoretical ones closely. Results for aqueous sodium oleate on glass plates did not check the theoretical values as closely as did the results for other liquids.

8. An edge is defined as being made up of a number of infinitesimal surfaces of intersection or as a surface of transition between two planes; an edge changes direction rapidly for each infinitesimal advance across it.

9. An explanation of why a liquid is reluctant to cross a convex edge is given; the liquid's deportment depends on the dip of the face it meets after crossing the edge.

10. An edge was designed for rendering a plate most floatable; a groove was ground, on the upper surface just inside the edge of such section that the reentrant angle (solid) was equal to or less than the contact angle of the liquid (on which the plate is to rest) with the plate. With this design there is obtained the maximum, physically possible, height of the liquid profile, and therefore maximum floatability.

11. When a prismatic body (heavier than water) floats on water or any other liquid, the forces due to the liquid displaced by the volume of the body and to the hydrostatic head acting upon the lower surface of the solid are the principal ones in balancing the weight of the body; the edges of the body make a barrier along which the liquid forms a wall instead of flowing over the top of the body. The effect of this barrier vanishes only when the contact angle is zero.

12. The principle of edge effect explains why mineral floats away by film suspension in the gold sluices, on the concentrating table, and on the film-suspension flotation machine.

13. A liquid may make a small angle of contact against a plane face of a solid in massive form, and in turn make a large angle against the same material powdered and cemented on a plate.

14. The contact angle is closely related to the spreading power of a liquid on a solid; when it is zero, the liquid is said to spread on or wet the solid.

15. Amalgamating, tinning, galvanizing, and leading are examples of spreading. As spreading takes place, the inequality of the interfacial tensions acting in any one of these is indicated.

16. Minute traces of contaminants often suffice to prevent the spreading of a liquid on a solid.

17. A consideration of the subject of spreading is essential in obtaining efficient coal dust sprays, detergents, animal dips, horticultural sprays, etc.

PUBLICATIONS ON FLOTATION.

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PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

TECHNICAL PAPER 135. Bibliography of recent literature on flotation of ores, January to June, 1916, by D. A. Lyon, O. C. Ralston, F. B. Laney, and R. S. Lewis. 1917. 20 pp.

TECHNICAL PAPER 149. Answers to questions on the flotation of ores, by O. C. Ralston. 1917. 30 pp.

TECHNICAL PAPER 176. Bibliography of recent literature on flotation of ores, July 1 to December 31, 1916, by D. A. Lyon, O. C. Ralston, F. V. Laney, and R. S. Lewis. 1917. 27 pp.

TECHNICAL PAPER 182. Flotation of chalcopyrite in chalcopyrite-pyrrhotite ores of southern Oregon, by W. H. Coghill. 1918. 13 pp., 1 fig.

TECHNICAL PAPER 283. Tests of low-grade and complex ores in Colorado, by W. H. Coghill and C. O. Anderson. 1923. 67 pp., 4 figs.

TECHNICAL PAPER 301. Proposed method for reducing mineral waste in the Wisconsin zinc district, Wisconsin, by W. H. Coghill and C. O. Anderson. 1922. 66 pp.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 154. Mining and milling of lead and zinc ores in the Missouri-Kansas-Oklahoma zinc district, by C. A. Wright and H. A. Buehler. 1918. 134 pp., 17 pls., 13 figs. 30 cents.

TECHNICAL PAPER 200. Colloids and flotation, by F. G. Moses. 1918. 24 pp. 5 cents.